X-RAY FLUORESCENCE AS A METHOD OF CHARACTERIZING INORGANIC PIGMENT PATTERNS IN ART

A Thesis

by

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ABSTRACT

In the fall of 2014 and the spring of 2015, 33 paintings by the Texas painter Julian Onderdonk (1882-1922) were analyzed using a portable X-ray fluorescence detector. The resulting spectral information revealed the elemental composition of the pigments used by Onderdonk and how they varied through his career. Using these spectra, elemental patterns were established that differentiated the paintings based on three major periods in Onderdonk's career, and undated works were matched with these patterns to assign them to a likely date range. The technique for identifying the pigments used in this thesis is useful for the analysis of both art and archaeological materials, and can be employed to substantiate stylistic associations of design between objects and to identify fraudulent items.

DEDICATION

For Mom

ACKNOWLEDGEMENTS

First and foremost I am eternally grateful to my committee chair Dr. Donny Hamilton for the tremendous opportunities and support he has afforded me while I have been at Texas A&M. I am also extremely grateful to my other committee members, Dr. Kevin Crisman and Dr. Emile Schweikert for their support and input. This study would not have been possible without the incredible help and support of James and Kimel Baker, who not only set me started on this path, but have singlehandedly facilitated access to every single one of the paintings analyzed and have proven to be a tremendous source of information and ideas. Thank you both from the bottom of my heart. Special thanks to Catherine Hastedt of the Stark Gallery at Texas A&M, Amy Fulkerson from the Witte Museum in San Antonio, and Meg Nowack, the curator of the National Trust Villa Finale home in San Antonio for giving me permission to come into their respective galleries and shoot X-rays at their collections. I am also very grateful to Dr. Jeffery Ferguson at the University of Missouri Research Reactor for taking the time to help me understand the principals of X-ray fluorescence above what I was able to glean from the excellent workshop given by Dr. Lee Drake from Bruker Elemental. Everything I have learned so far has been a product of the excellent academic environment in the Anthropology Department of Texas A&M, and I am grateful to the entire faculty, staff, and students I have had the pleasure of collaborating with so far.

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SECTION 1: INTRODUCTION

In October of 2014, art collector and author James Baker and his wife Kimel Baker requested the Center for Maritime Archaeology and Conservation's (CMAC) Conservation Research Laboratory (CRL), (both located within the Anthropology Department's Nautical Archaeology Program at Texas A&M University) to analyze two nearly identical paintings of a harbor scene using portable X-ray fluorescence (pXRF). One of the paintings was signed Chas. Turner, and the other, Emile Gruppe. James Baker had recently published a book on his discovery that the 19th-century Texas impressionist painter Julian Onderdonk had painted under the pseudonym of Chas Turner for a number of years, and they wanted to compare the two paintings to see if it was possible that they had both been painted by the same artist. The comparative analysis proved conclusively that they had not. Encouraged by the results, the Bakers returned in mid-November of 2014 with 12 additional paintings.

After analyzing 13 of Onderdonk's paintings, a pattern began to emerge in the pigment patterns that he used during different periods of his career. In March of 2015, in cooperation with the Witte museum and the Villa Finale historic trust in San Antonio, Texas, as well as the Stark Gallery at Texas A&M University, 20 more of Onderdonk's paintings (for a total of 33) were analyzed with the goal of demonstrating that pXRF can be used to establish a spectral pattern in pigment choices through time for a particular artist. This non-destructive testing can be used to associate undated works with dated ones, to lend insight into the life of the artist, and even to identify areas of repair or fraudulent paintings.

SECTION 2: HISTORICAL BACKGROUND

Robert Julian Onderdonk (1882-1922), commonly known as Julian Onderdonk, was an American Impressionist painter from San Antonio, Texas. He is best known today for his vibrant, sprawling depictions of bluebonnet-filled Texas landscapes, and his paintings, which routinely auction for six figure sums, have been showcased in museums and art galleries around the country, and have even adorned the White House walls during the presidency of George W. Bush from the years 2000-2008 (Yoo 2015, Kahn 2014). Onderdonk painted prolifically nearly his entire life, starting at the age of two in 1885 and ending with his untimely death in 1922 at the age of 40 (Baker 2014:1; Rudolph 2008:149). Onderdonk began to learn to paint as a young child, both on his own and from his father Robert Onderdonk, a professional artist and art instructor (Rudolph 2008:149). In January of 1901, Julian Onderdonk borrowed money from his neighbor George Beddell Moore and moved to New York City to attend classes at the Art Students League. This debt would follow Onderdonk for the next seven years, causing significant financial strain. The portrait that Onderdonk painted of Moore in 1905 is included in this study (Rudolph 2008:21; Baker 2014:143).

Onderdonk stayed in New York for nine years, and painted constantly, often producing one or more paintings every single day over that period (Baker 2014:7). He sold his work the best he could, but like many aspiring artists in New York City, he struggled financially. In 1904, Onderdonk began a business relationship with someone known only as Chas. Tunison, (likely either Charles or Chase), who paid Onderdonk to paint and then sold the paintings on his own. The paintings that Onderdonk did for

Turner were signed under a pseudonym of Chas. and Chase Turner. The Turner paintings are indistinguishable from the work that Julian Onderdonk signed with his own name; often they are of the exact same subjects and scenes. By having him use a pseudonym and selling the work without his presence, Tunison was able to keep Onderdonk reliant on him without any alternative source of income for at least four years. By 1908, Onderdonk had either completely eliminated or at least severely limited his relationship with Tunison and began signing his own name to his work once again.

In the fall of 1908, George Beddell Moore died and released Onderdonk from his debt in his will (Baker 2014:143). The next year, Onderdonk and his family returned to Texas, settling back in San Antonio. Very shortly after returning, Onderdonk once again left for New York in the spring of 1910, though this was followed by a hasty return in the November of 1910 when he learned that his wife left him upon hearing rumors that he was having an affair (Baker 2014:151-154). Onderdonk continued to paint, and sold his work and taught at the Wasson School in San Antonio to support himself and his family. His time in New York greatly improved his technical abilities, but it was not until his return to Texas that he was inspired to create the famous bluebonnet scenes he is now famous for. He created more than one thousand paintings during his short life, and many of them are without a known date or context apart from the subject matter.

SECTION 3: GOALS AND METHODOLOGY

Knowing Julian Onderdonk's biographical information was keenly important to the design of this study. Of the 33 paintings analyzed, ten have no dates assigned and two have only tentative dates based on associations with similar, dated works. In Baker's Julian Onderdonk in New York: The Lost Years – The Lost Paintings, analysis of Onderdonk's signature reveals a shift in style between 1906 and 1908, allowing many of the undated works to be grouped to a general date range. The paintings analyzed in this study cover the three major periods of Onderdonk's work, ranging from his pre-New York phase in 1899, through his time in New York from 1901 to 1909, followed by his time back in Texas from 1909 up to the very last painting he completed before his death in 1922. The goal of this study is to attempt to identify pigment markers that can further refine these groupings, and to develop pigment patterns that are unique to certain periods of Onderdonk's career. By focusing on a single artist, the possibility of establishing these patterns is greatly enhanced compared to looking at broad swaths of pigments used by painters in a particular region or a time period.

For each painting analyzed, several small areas, or points, were chosen to examine based on pigment hue, apparent homogeneity of the paint, and the thickness of the paint. Once the data was collected for each point in a graphical format called a spectrum, the spectra for the different points were compared to one another in order to attempt to isolate the constituent building blocks responsible for a particular hue. In some cases, a distinct pigment color was determined, and in others, the colors were

clearly a blend of two or more colors. Though some of the pigments analyzed remain ambiguous, for the most part this method of analysis was successful.

SECTION 4: X-RAY FLUORESCENCE: A PRIMER

Understanding the data obtained with X-ray fluorescence spectroscopy (XRF) necessitates an understanding of how and why the instrument obtains data, and what kind of data it receives. The chemical testing techniques available for the archaeologist or conservator today can be separated into two general categories: quantitative measurements and qualitative measurements. Quantitative measurements tell you how much of something there is in an object being tested, and qualitative measurements tell you what is in the object being tested, not how much of it there is. Quantitative measurements of intensity-energy interactions in the electromagnetic scale are known collectively as spectrophotometry, and include techniques such as atomic spectroscopy and neutron activation analysis (NAA). These tests determine not only the presence of atoms, but also the mass (M) of the individual elements present in a sample (Artioli 2010:29). Qualitative measurements like mass spectroscopy and XRF detect the presence of an element and its relative quantity between samples, but not mass (Russ 1984:17). Calibrating the spectral information gained through qualitative measurements with spectral information obtained through a quantitative measurement like NAA can produce quantitatively calibrated data, but this was not needed or practical for the purpose of this study.

Before understanding the principals by which XRF detection operates, it is first necessary to understand what X-rays are. Put simply, they are a high energy, short wavelength electromagnetic radiation that is generated outside of the nucleus of an atom (Russ 1984:1). This is an important distinction; the energy and wavelengths of X-rays

can overlap with those of gamma (γ) rays, but γ-rays are generated from within the nucleus of an atom.

Taking a step back, each atom, the individual building blocks of molecules, is composed of a nucleus in the center and orbiting electrons (Figure 1). The nucleus contains neutrons, which have no electrical charge, and protons, which have a positive

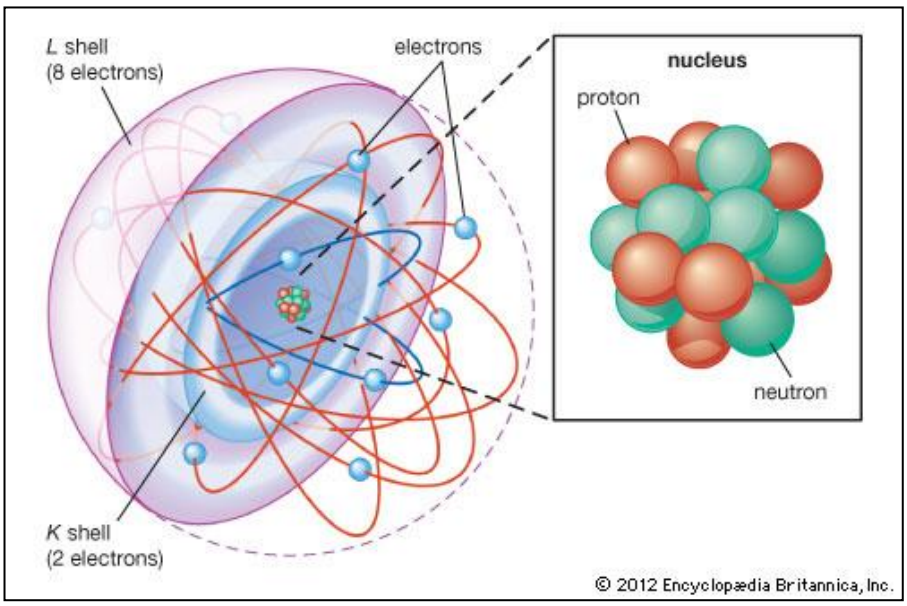

Figure 1. Structure of an atom. From: Encyclopedia Britannica.

charge. The number of protons in the nucleus is known as the atomic number (Z number), and this determines the chemical properties of that atom, or which type of atomic element it is. If an atom has 82 protons in its nucleus, it is a lead atom. The number of neutrons in the nucleus determines atomic weight, or the isotope, of a particular element.

Orbiting the nucleus are negatively charged electrons, and these electrons orbit the nucleus at different levels, known as shells. If the negative charge of all of the electrons orbiting the nucleus is equal to the positive charge of all of the protons, the atom is neutral. If the charge is unbalanced, then the atom will have an overall positive or negative charge; atoms with a charge are called ions. Interactions with other electromagnetic energy can change the number of electrons than an atom has in orbit, thereby affecting its charge. Low frequency and long wavelength electromagnetic radiation like infrared light and radio waves are non-ionizing, meaning that they do not have enough energy to remove electrons from around the orbit of an atom. High frequency, short wavelength electromagnetic radiation like γ-rays and X-rays are types of ionizing radiation, and they do have the energy necessary to remove electrons from the orbit of an atom (Russ 1984:1-2). When an ionizing interaction occurs that causes one of the electrons in orbit around the nucleus of an atom to be ejected, electrons from other orbits will fall in to fill the vacancy, and the electron filling this vacancy will emit a certain amount of X-Ray energy proportional to the number of protons in the nucleus. (Russ 1984:2). The purpose of an XRF detector is to intentionally ionize an atom by exposing it to X-rays, and then read the emitted X-ray energy that occurs when electrons fall in to replace ejected electrons.

X-rays are produced by passing an electrical current through an X-ray tube. This electrical current is comprised of negatively charged electrons moving along a conductive wire. The tube contains a negatively charged cathode filament, which produces high energy electrons, and a target anode with a positive charge that attracts

and accelerates the negatively charged electrons produced by the cathode (Russ 1984:208). These accelerated high energy electrons hit the target material and can either eject an electron orbiting the nucleus of an atom in the target, or be deviated from their path by coming too close to the nucleus of an atom in the target. If an electron is ejected, (the atom is ionized), a higher orbit electron moves to the vacancy to replace the missing electron, and the energy difference between the two orbits is released in the form of an X-ray (Russ 1984 2:210). This X-ray's energy is dependent on the number of protons in the nucleus of that atom, and is thereby characteristic of a particular element. If the electron is deviated from its path by travelling too close to the atom, it will lose some of its energy, and emit some of that lost energy as an X-ray. This is known as bremsstrahlung radiation (Russ 1984:7).

XRF is an analytical tool that uses a focused beam of X-ray photons to intentionally eject electrons in orbit around an atom and produce characteristic X-rays via ionization. The energy of these X-rays is then detected by the sensor in the XRF, and the voltage and the number of pulses are counted and displayed on a graph called a spectrum. Figure 2 shows a typical spectrum with XRF data. The X axis shows the voltage of the incoming X-rays in kilo electron volts (keV), and the Y axis shows the intensity of the peak, or the number of pulses received.

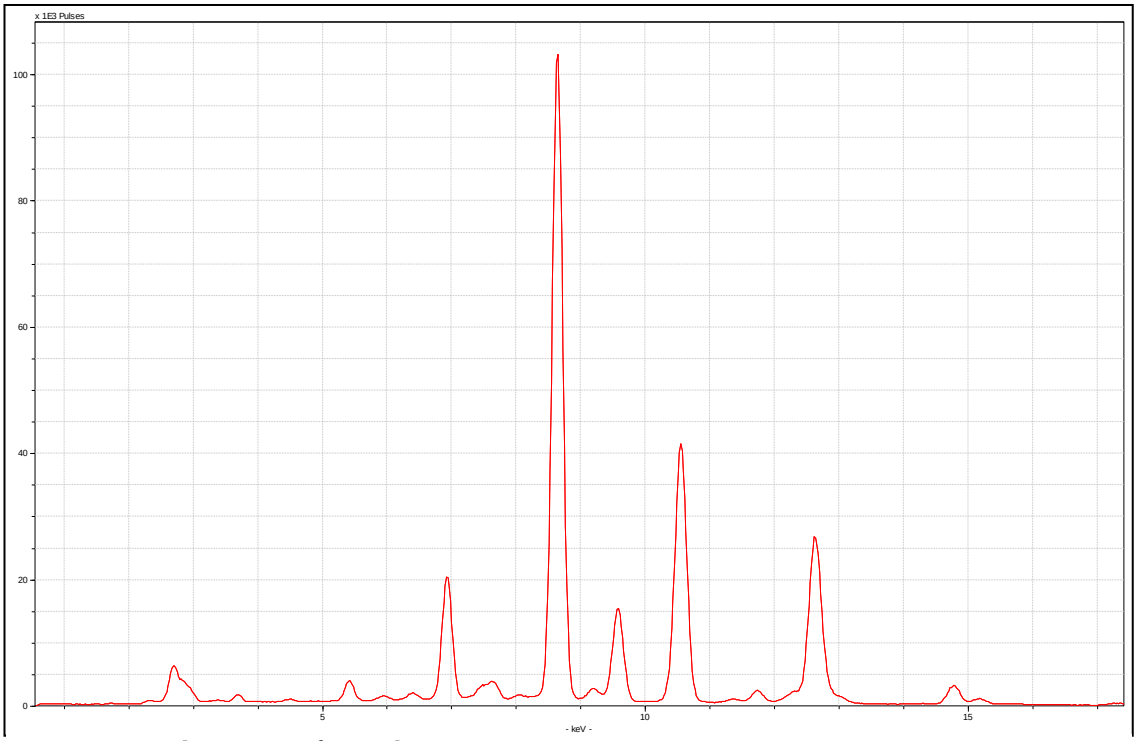

Figure 2. Typical spectrum of XRF data

The voltage indicates which elements are present, and the intensity of the peak indicates relative mass. The mass is only relative between samples; a higher peak of an X-ray dense element compared to an X-ray transparent element does not indicate that there is more of one than the other, only that more X-ray interactions took place.

As mentioned above, electrons orbit atoms in distinct levels, or shells (Figure 1). Depending on which shell the electrons are ejected from and which shell their replacement electrons come from, the energy of the characteristic X-ray released by ionization can vary. The innermost orbit is known as the *K* shell, the 2nd orbit is known as the *L* shell, the third the *M* shell and so on (Russ 1984:2). If an electron from the inner-most orbit (the *K* shell) is ejected, and an electron from the second orbit (*L* shell) moves in to take its place, the X-ray emitted gives an energy peak known as a *K*α peak.

If the *K* shell vacancy is filled with an electron from the *M* shell, the X-ray peak emitted is known as a *K*β peak. Likewise, if an *L* shell electron is ejected and replaced with an *M* shell electron, the energy of the X-ray released is known as *L*α, and if it is replaced by an *N* shell electron, it is an *L*β peak. For the *L, M, N* (and other) shells, there are also sub-shells; an electron moving from a particular subshell of *M* to a particular subshell of *L* is designated as *L*α-1, *L*α-2, and so on (Markowicz 2002:7).

In high Z number elements like barium or lead, the *K*α and *K*β energy peaks are too high to detect with an XRF detector. In these cases, the lower energy *L* peaks are used to identify the presence of these elements. In low Z number elements like phosphor or calcium, the *L* energy peaks are too low to detect, and only the higher energy *K* peaks are visible. In the mid-range Z elements like rhodium through iodine, both *K* and *L* energy peaks are detected. Organic elements such as hydrogen, carbon, nitrogen, and oxygen interact with the X-rays, but their characteristic energies are too low to even pass back through the sample being tested or the air between the sample and the detector, and are therefore invisible to conventional energy dispersive XRF detection (Russ 1984:179).

Because high Z number elements are detected with *L* energy peaks and low Z number elements are detected with *K* peaks, there is the possibility that a sample being analyzed will have elements with *L* and *K* peaks overlapping. For the high Z number element lead (Pb), the Kα emission peak is 74.969KeV. Because the *K* energy peaks are too high to detect, the *L* energy peaks are used to identify the presence of lead. The *L*α energy peak for lead is 10.551 KeV, well within range of XRF. However, the Lα energy

peak for lead is very similar to the *K*α energy peak for arsenic (As), which is at 10.543KeV. If a sample contains both lead and arsenic, the lead Lα peak can mask the Kα peak of arsenic. Conversely, the Kα peak for arsenic can exaggerate the intensity of the Lα peak of the lead. Because of this, it is crucial that the β peaks and all of the sub-shell peaks for each element are identified when associating a spectral signature with an element.

SECTION 5: INTERPRETING THE PXRF DATA

Apart from the desired characterizing X-ray fluorescence of a sample material, there are many more energy interactions which can obscure the clarity of the data being received during pXRF detection. Not every X-ray photon emitted from the pXRF goes exactly where it is intended, and not every X-ray photon emitted has enough energy to cause an atom to eject an electron. X-rays are emitted from an X-ray tube in much the same way that visible light is emitted from a flash light. The photons are focused and directed via a mechanism in the X-ray tube called a collimator, but once the photons are produced, there is only so much that can be done to direct the beam. Using the analog of a flash light, if you shine a flash light at different types of material, the light can either pass through the material, be absorbed by the material, or reflect off of it, and rarely does only one of these responses occur. In much the same way, X-rays coming out of the XRF can either pass through the sample, reflect off of it, or be absorbed. Along with these possibilities, the X-rays can also interact with the materials in the instrument, react more than once with an element in the sample, or react with more than one element in the sample (Russ 1984, 69-70, 81).

In order to eject an electron from orbit around an atom, the incoming X-ray photon needs to have enough energy to do so. When this high energy X-ray photon ejects an electron, those ejected electrons often have enough energy to interact with other atoms. When the high energy electrons hit the atoms in the material being tested, some pass near the positively charged nucleus of these atoms and slow down and change direction, emitting X-rays equivalent to the energy they lost. This phenomena, known as

bremsstrahlung radiation, causes a broad range of X-ray energies to be back scattered back into the detector (Russ 1984, 7).

Along with this, some of the X-rays travelling from the XRF to the sample are reflected off of the material. If they are reflected with no loss of energy, this is known as Rayleigh scattering. If the X-rays are reflected but they lose some of their energy in the process, this is known as Compton's scattering. Bremsstrahlung radiation, or back scatter, along with Rayleigh and Compton's scattering all create background noise in the data received during analysis (Guthrie and Ferguson, 2012). In addition to background radiation, sometimes the incoming pulses of X-rays from the sample material enter the detector at exactly the same time, which is known as a sum peak. In the case of a sum peak, the detector might display one *K*α count at 16keV when it was actually two *K*α's at 8keV entering at the same time, or a *K*α of 10keV and a *K*β of 6keVarriving at the same time (Guthrie and Ferguson, 2012).

All of these phenomena can be accounted for during analysis by the end user, and many of them can be minimized by adjusting the voltage, current, and utilizing various filters with the XRF. Adjusting the voltage allows the instrument to only fluoresce certain elements, allowing elements with overlapping *K* and *L* peaks to be somewhat isolated from one another. Along with this, filters composed of different materials can be utilized to absorb certain X-rays that can interfere with the spectral peak of the elements being looked for. If a sample was being analyzed for the presence of chlorine (Cl), which has a *K*α-1 peak at 2.6220 KeV, the voltage would be dropped so as to not readily fluoresce higher Z number elements with *L* and *M* peaks in that range. If the XRF being

used had a rhodium (Rh) target in its X-ray tube, a filter would have to be used to block the rhodium *Lα* peak at 2.6968 KeV from obscuring the chlorine. If a thin titanium (Ti) filter is placed in the path of the XRF window, the rhodium X-rays will be absorbed, and titanium will fluoresce instead at 4.5122 KeV. Though this would allow for the identification of the presence of chlorine, it would be inappropriate if looking for titanium (Speakman 2012, 13).

SECTION 6: THE BRUKER TRACER III-SD

The pXRF detector used for this study was a Bruker Tracer III-SD, (pictured in figure 3 below), owned and operated by the CRL in the department of Anthropology at Texas A&M University. The Tracer III-SD is a silicone drift, energy dispersive XRF detector. Silicone drift detectors are capable of a high resolution at a high count rate without the need for the liquid nitrogen cooling systems that was necessary for older systems. The Tracer III-SD has a rhodium target, a thin polymer window, and has a typical resolution of 145eV at 100,000 counts per second (cps). The max voltage is 40kV, and it has a vacuum pump attachment to remove air from the device in order to enhance light element detection (Bruker 2015).

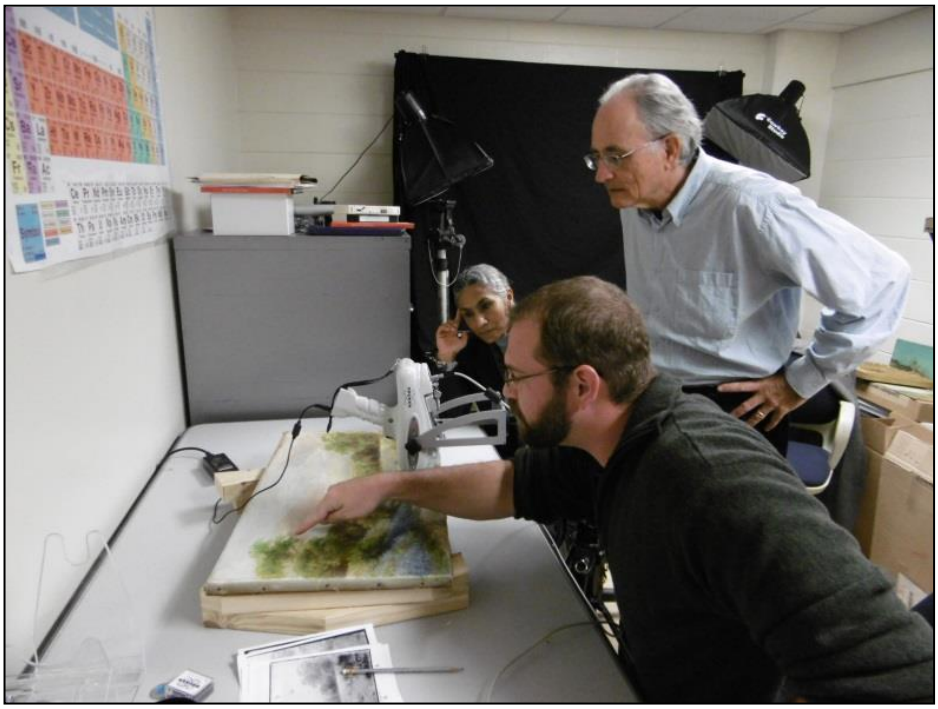

Figure 3. The author (foreground) with James and Kimel Baker analyzing Large Bluebonnet Landscape with the Bruker Tracer III-SD. Photo courtesy of Dr. Donny Hamilton.

The spectral graph data was acquired from the Tracer III-SD using either a laptop or a tablet running Bruker's S1PXRF software version 3.8.30, and these spectra were analyzed using Bruker's ARTAX software version 7.4.0.0. The paintings were analyzed with the vacuum pump running to maximize the detection of low Z number elements, though the effectiveness of the vacuum was mitigated by the inability to make direct contact between the pXRF window and the painting surface for fear of damaging the paintings. The vast majority of the paintings were analyzed on a tabletop with the XRF mounted on a tripod, though four paintings from Villa Finale in San Antonio, Texas and two from the Stark gallery at Texas A&M University were analyzed holding the pXRF by hand while the paintings remained hanging on the wall.

SECTION 7: PAINTING ANALYSIS

This section is organized as a series of individual subsections that analyze the spectra of the points for each painting to determine their composition. To do this, each of the individual points for a particular painting were loaded into the ARTAX software and examined one at a time. The first step was to note which X-ray peaks were seen for each point, listing the elements present and then cross referencing these elements with pigment possibilities in Eastaugh et al's Pigment Compendium (2008), Wehte's The Materials and Techniques of Painting (1975), and Roy's Artists' Pigments: A Handbook of Their History and Characteristics (1986). The historical information about the various pigments in these texts proved especially useful, as it was not necessary to consider pigments that had been developed and manufactured after Onderdonk's death in 1922.

The second step was to compare the spectrum of each point to the spectra of the others to identify elemental similarities and differences between the different colors. All of the paintings have a base coat or primer put down before the scene is painted, and this is generally very clearly identifiable as a consistent peak across all points. The peaks for the elements that are unique to the color of a particular point were then matched against the list of possible pigments, and the most parsimonious fit for the pigments chemical makeup was assigned.

All of the elements encountered in this study are listed below in table 1 with their abbreviations for clarity when conveying chemical formulas and interpreting the graphs. Table 2 lists the more commonly observed pigments and their formulas. It should be noted that the scale of the spectral graphs are optimized to emphasize the elements

present in each sample. The figures in this section are not drawn to a consistent scale, and therefore peak intensities between figures cannot be compared to one another in a meaningful way. For precise photon counts of a specific scan, .csv files of the results, or copies of the Bruker .pdz files, contact the author.

There are two major drawbacks to using pXRF to analyze pigments. The first is that the pXRF is unable to detect the use of organic materials. This means that the analysis presented here are likely incomplete. A number of organic based pigments exist and are frequently used, but given the inability of the instrument to detect them, they were necessarily ignored for this study. In some cases, it is noted that due to a lack of otherwise compelling data, organic pigments are the most likely source of a color, but this is inference based on a lack of evidence. The second drawback is that the XRF is unable to detect chemical structure. The non-organic elemental composition is read, but what each element is bonded with is not (Cesareo et al 2008, 206). Many elements are present in a wide variety of pigments. Iron (Fe) for example can be found in hematite red, orange and yellow ochre, and even Prussian blue. When each pigment point is analyzed, the hue of the point must be taken into account when attempting to find the best chemical fit for the elements present.

Name	Abv.	Name	Abv.	Name	Abv.	Name	Abv.
Actinium	Ac	Erbium	Er	Molybdenum	Mo	Antimony	Sb
Silver	Ag	Einsteinium	Es	Meitnerium	Mt	Scandium	Sc
Aluminum	Al	Europium	Eu	Nitrogen	N	Selenium	Se
Americium	Am	Fluorine	F	Sodium	Na	Seaborgium	Sg
Argon	Ar	Iron	Fe	Niobium	Nb	Silicon	Si
Arsenic	As	Flerovium	Fl	Neodymium	Nd	Samarium	Sm
Astatine	At	Fermium	Fm	Neon	Ne	Tin	Sn
Gold	Au	Francium	Fr	Nickel	Ni	Strontium	Sr
Boron	B	Gallium	Ga	Nobelium	No	Tantalum	Ta
Barium	Ba	Gadolinium	Gd	Neptunium	Np	Terbium	Tb
Beryllium	Be	Germanium	Ge	Oxygen	O	Technetium	Tc
Bohrium	Bh	Hydrogen	H	Osmium	Os	Tellurium	Te
Bismuth	Bi	Helium	He	Phosphorus	P	Thorium	Th
Berkelium	Bk	Hafnium	Hf	Protactinium	Pa	Titanium	Ti
Bromine	Br	Mercury	Hg	Lead	Pb	Thallium	Tl
Carbon	C	Holmium	Ho	Palladium	Pd	Thulium	Tm
Calcium	Ca	Hassium	Hs	Promethium	Pm	Uranium	U
Cadmium	Cd	Iodine	I	Polonium	Po	Ununoctium	Uuo
Cerium	Ce	Indium	In	Praseodymium	Pr	Ununpentium	Uup
Californium	Cf	Iridium	Ir	Platinum	Pt	Ununseptium	Uus
Chlorine	Cl	Potassium	K	Plutonium	Pu	Ununtrium	Uut
Curium	Cm	Krypton	Kr	Radium	Ra	Vanadium	V
Copernicium	Cn	Lanthanum	La	Rubidium	Rb	Tungsten	W
Cobalt	Co	Lithium	Li	Rhenium	Re	Xenon	Xe
Chromium	Cr	Lawrencium	Lr	Rutherfordium	Rf	Yttrium	Y
Cesium	Cs	Lutetium	Lu	Roentgenium	Rg	Ytterbium	Yb
Copper	Cu	Livermorium	Lv	Rhodium	Rh	Zinc	Zn
Dubnium	Db	Mendelevium	Md	Radon	Rn	Zirconium	Zr
Darmstadtium	Ds	Magnesium	Mg	Ruthenium	Ru		
Dysprosium	Dy	Manganese	Mn	Sulfur	S		

Table 1. Element names and their abbreviations From: Jefferson Lab www.jlab.org.

Pigment name	Chemical Formula	Date
Barium white	$BaSO_4$	Used in Antiquity, manufactured from 1830 in France
Titanium white	TiO_2	First produced in 1821, but not available to artists until the late 1920s
Lead white	$Pb_3(CO_3)_2(OH)_2$	At least as old as 1500BC in Egypt and Greece
Zinc white	ZnO	First produced as early as 1782, mass produced by 1835
Realgar red	As_4S_4	Used in antiquity
Hematite (or ochre)	Fe_2O_3	Used since prehistoric times
Red lead (minium)	Pb_3O_4	Used since the Roman empire
Vermillion red	HgS	Used in antiquity
Lemon yellow	$BaCrO_4$ or $SrCrO_4$	Discovered in 1809
Cadmium yellow	CdS	Discovered in 1817
Chrome yellow	$PbCrO_4$	Discovered in 1809
Zinc yellow	$ZnCrO_4$	Discovered in 1809
Chromium oxide green	Cr_2O_3	Discovered in 1809
Cobalt green	Co – doped zinc oxide	Discovered in 1809
Verdigris green	$Cu(C_2H_3O_2)_2 \bullet {}_2Cu(OH)_2$	Used in antiquity
Azurite blue	$Cu_3(CO_3)_2(OH)_2$	Known since the 15th century, manufactured artificially since the 18th century
Cerulean blue	$CoO \bullet SnO_2$	Introduced in 1821, reintroduced in 1860
Cobalt blue	Co – doped alumina	Discovered in 1775, manufactured from 1804 for artists
Egyptian blue	$CaCuSi_4O_{10}$	Used in antiquity
Han blue	$BaCuSi_2O_6$	Discovered in 1859
Prussian blue	$(Fe_4[Fe(CN)_6]_3)$	Known since 1704, manufactured from 1870 for artists
Smalt	Co – doped Si glass	Known since mid-16th century
Cobalt Violet	$Co_3(PO_4)_2$ or $Co_3(AsO_4)_2$	Discovered in 1859

Table 2. Pigment names and chemical formulas (From Artioli 2010).

There is another inherent weakness in this study, though it has nothing to do with the XRF as a tool or the analysis done. It is the simple fact that Julian Onderdonk had no real reason to systematically adhere to a single type of paint. As an artist, Onderdonk's primary objective when selecting paints was more than just the chemical composition. In his 1975 book The Materials and Techniques of Painting, Kurt Wehlte describes 15 characteristics to consider when selecting a paint: appearance, chemical composition, texture, permanence (light fastness), compatibility with other pigments, fastness to media, miscibility, wetting (ability to dissolve in media), vehicle absorption, stability of consistency, tinting strength, hiding power, transparency, effects on unsaturated oils, and toxicity (Wehlte 1975, 57-68). It is likely that a formally trained artist like Onderdonk used similar criteria when selecting his paints. Luckily for the purpose of this study, Onderdonk was under significant financial pressure during a large portion of his career, and therefore would have been less likely to have the freedom of experimenting with new and untested paints.

Sunset November 1899

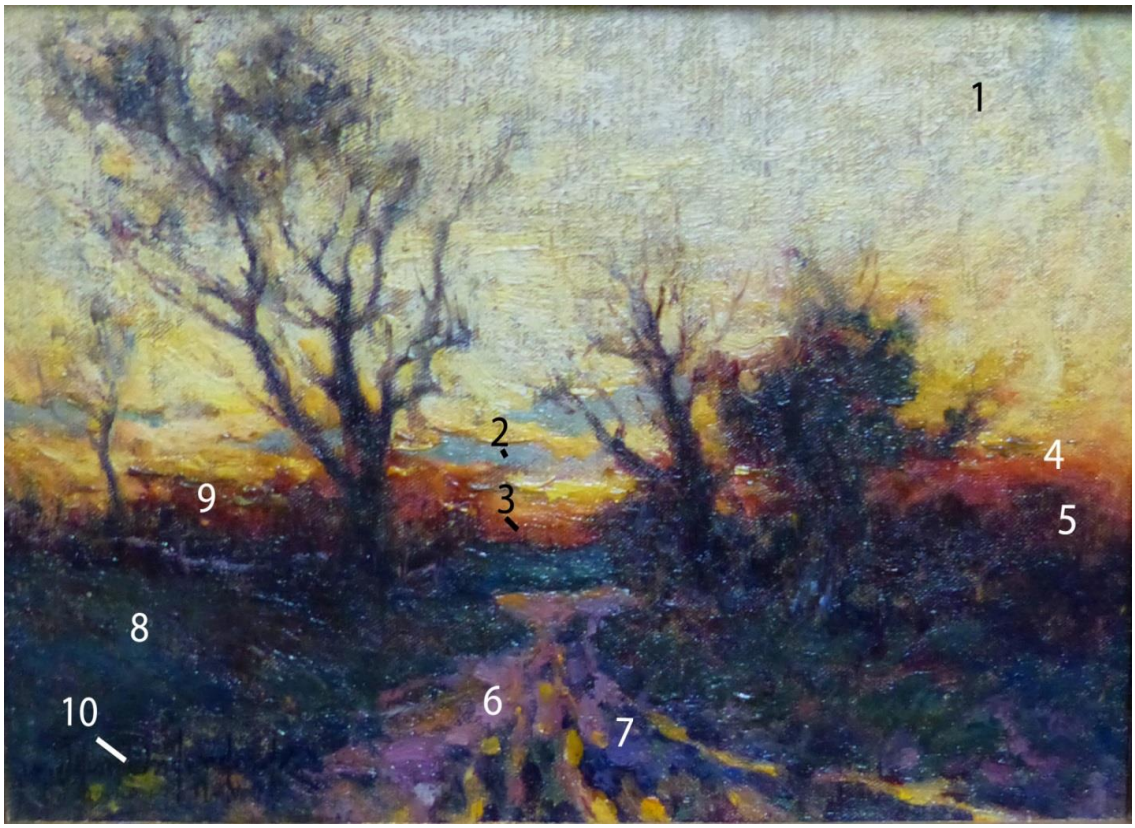

Figure 4. *Sunset November 1899*. 1899, Signed Julian Onderdonk, Oil on Canvas Board, 6.25in x 9.5in, James and Kimel Baker Collection, College Station, TX.

A total of 10 points were analyzed for *Sunset November 1899* (figure 4). Point 1 was the yellowish white in the sky, point 2 is the blue of the sky, point 3, four and nine are reds of the sky, point 5, 6, and 7 are violets, point 8 is dark green, and point 10 is the signature.

Yellow and White

The highest energy peak for Point 1 is lead (figure 5). It should be noted at the outset of these analyses that lead is excellent at interacting with X-rays; this is why lead shielding is commonly used to protect against accidental X-ray exposure. The implication of this on the following spectra is that when lead is present, it will often have a deceptively high energy peak. This does not necessarily indicate that there is a high concentration of lead present, only that the lead is interacting very successfully with the X-rays. This pigment is certainly a lead white, and the presence of cadmium suggests cadmium yellow was used as well.

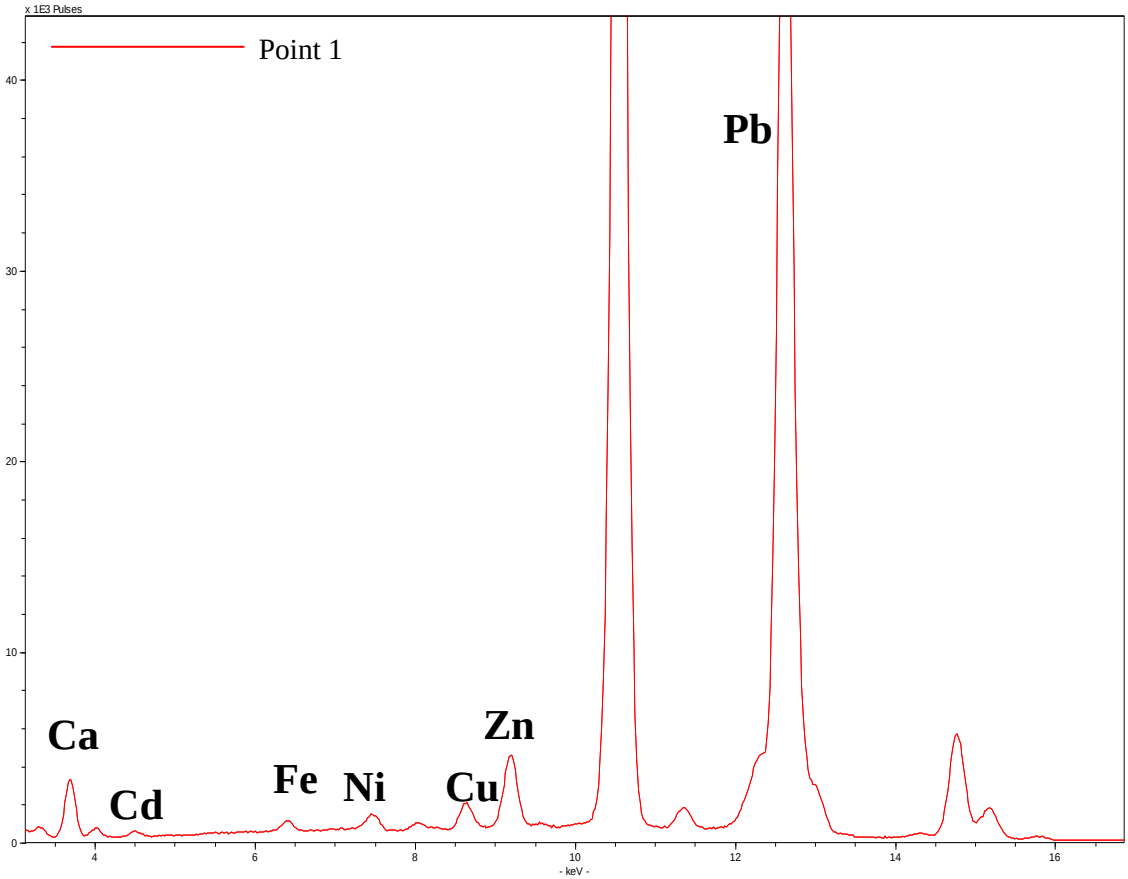

Figure 5. *Sunset November 1899*. Point 1, white.

Blue

Point 2 is the blue from the sky in the center of the picture (figure 6). There are energy peaks for calcium, chromium, cadmium, iron, copper, nickel, and lead. The copper could indicate azurite, and the iron could indicate Prussian blue, but given that point 8, the green analyzed below is copper based, and the lack of intensity for the iron peak, it seems likely that this blue is of organic origin or is a copper based blue.

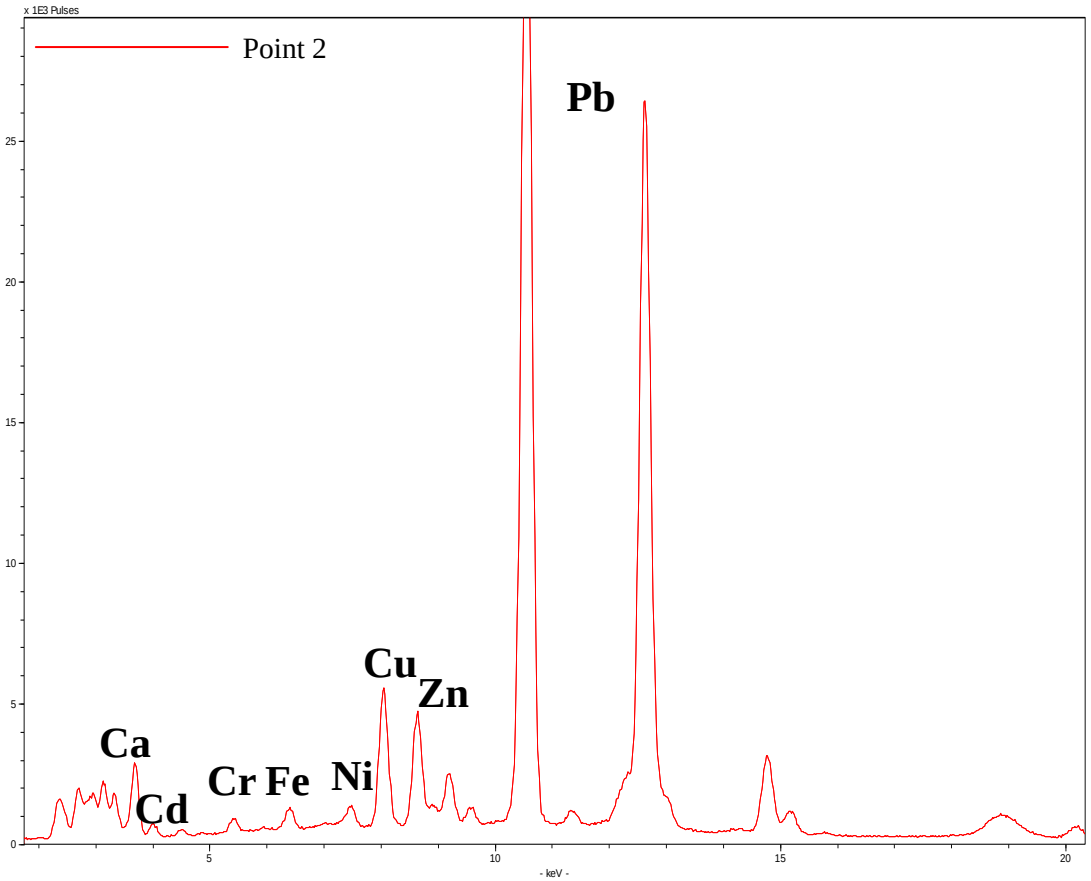

Figure 6. *Sunset November 1899*. Point 2, blue.

Red

Points 3, 4, and 9 are reds (figure 7) . Points 3 and 4 are obviously painted over yellow, and point 9 is quite dark and well blended with other colors. Comparing the three spectra, the differences among them are very informative. Point 9 has higher peaks for copper, zinc, cadmium, chromium and shares a high peak for calcium with point 4. Point 4 has the highest peak for calcium, and is very similar to point 3 for peaks chromium, copper, and zinc. Point 3 has the highest lead content. The only common element contained in all three of these points is iron. Given this, it is likely that the red is an iron based hematite pigment.

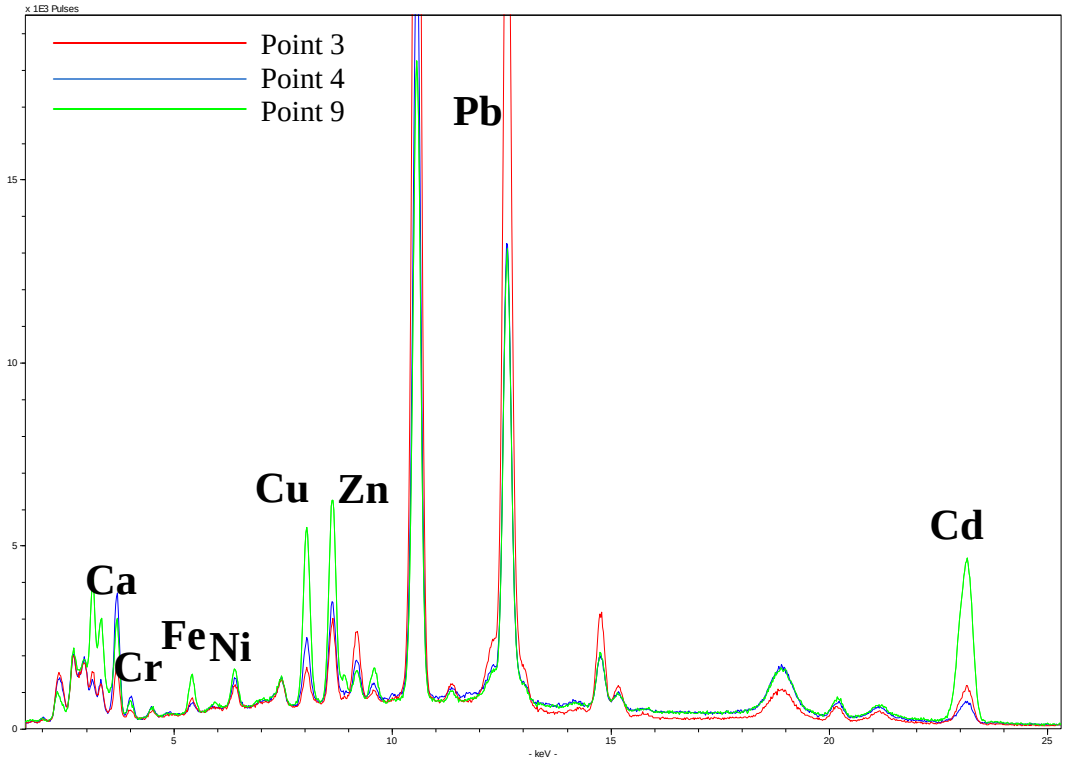

Figure 7. *Sunset November 1899*. Point 3, 4, and 9, reds.

Violet

Point 6 is the lightest and seemingly truest of the three violets analyzed. Point 7 is mixed heavily with the surrounding blue, and point 5 is very dark (figure 8). Starting with point 6, it is dominated by the peak of lead. There is a strong copper peak, though smaller than that of point 7. Given the strength of the lead signature, and the fact that it is the lightest shade, it stands to reason that the violet of point 6 was lightened with lead white. Point 7, mixed with the blue, has the strongest copper peak of the three. This might indicate the use of a copper based blue, given that there appears to be little obvious green in that area. The dark violet of point 5 has a strong calcium peak, as well as very subtle peaks for Al and silicon. The lead drowns out any sulfur that might be present, and given that the pXRF is not sensitive to sodium or oxygen, this could well indicate the use of ultramarine ($Na_3CaAl_3Si_3O_{12}S_n$), either as a blue or a violet. This painting will have to be re-analyzed with different settings to verify if this is the case or not.

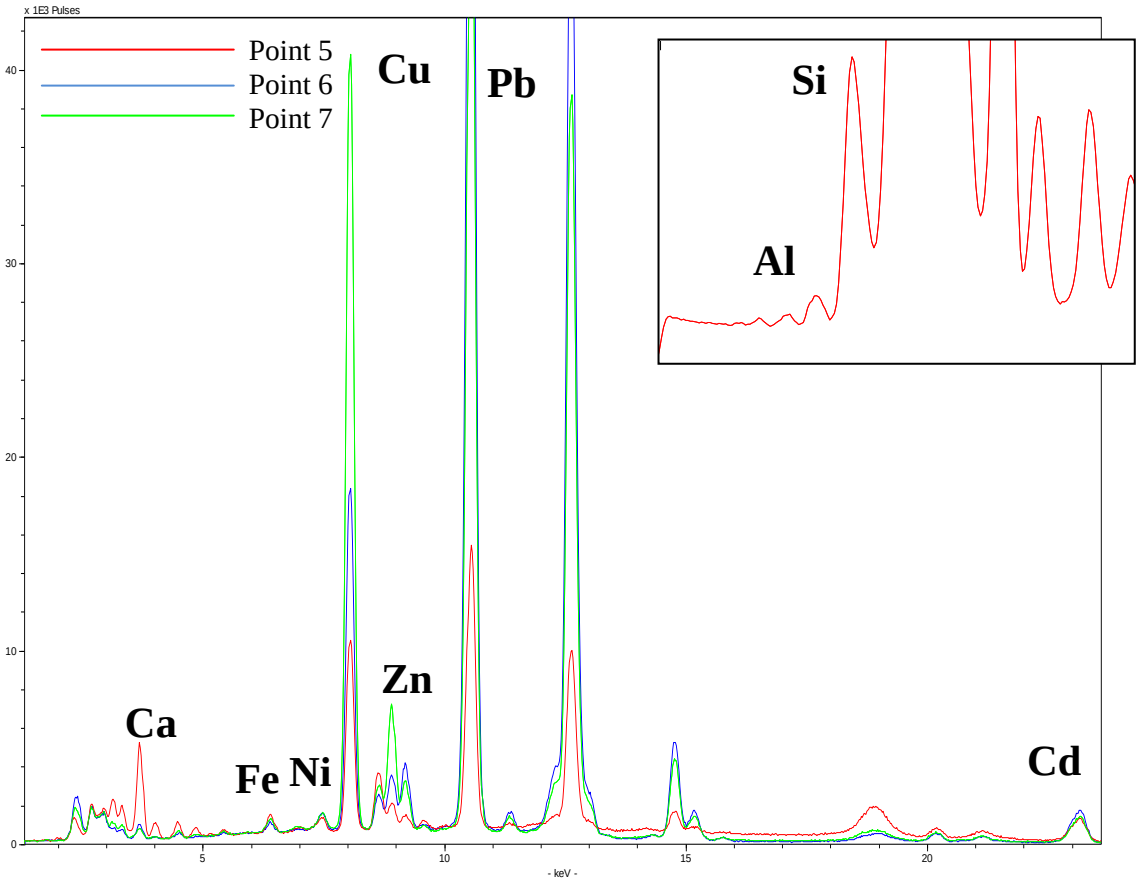

Figure 8. *Sunset November 1899*. Points 5-7, violets. Inset shows 1-3 keV.

Green

The green in point 8 is unambiguously copper-based, though it is not clear which one or more of the copper-based green pigments it is (figure 9). The most likely copper greens are atacamite ($Cu_2Cl(OH)_3$), malachite ($Cu_2(CO_3)(OH)_2$), or verdigris ($Cu(C_2H_3O_2)$). The other two, chrysocolla ($CuSiO_3$), and Egyptian green ($CaSiO_3$ and ground green glass) are not likely due to the lack of a peak for silicon, though it is possible that it is not being detected.

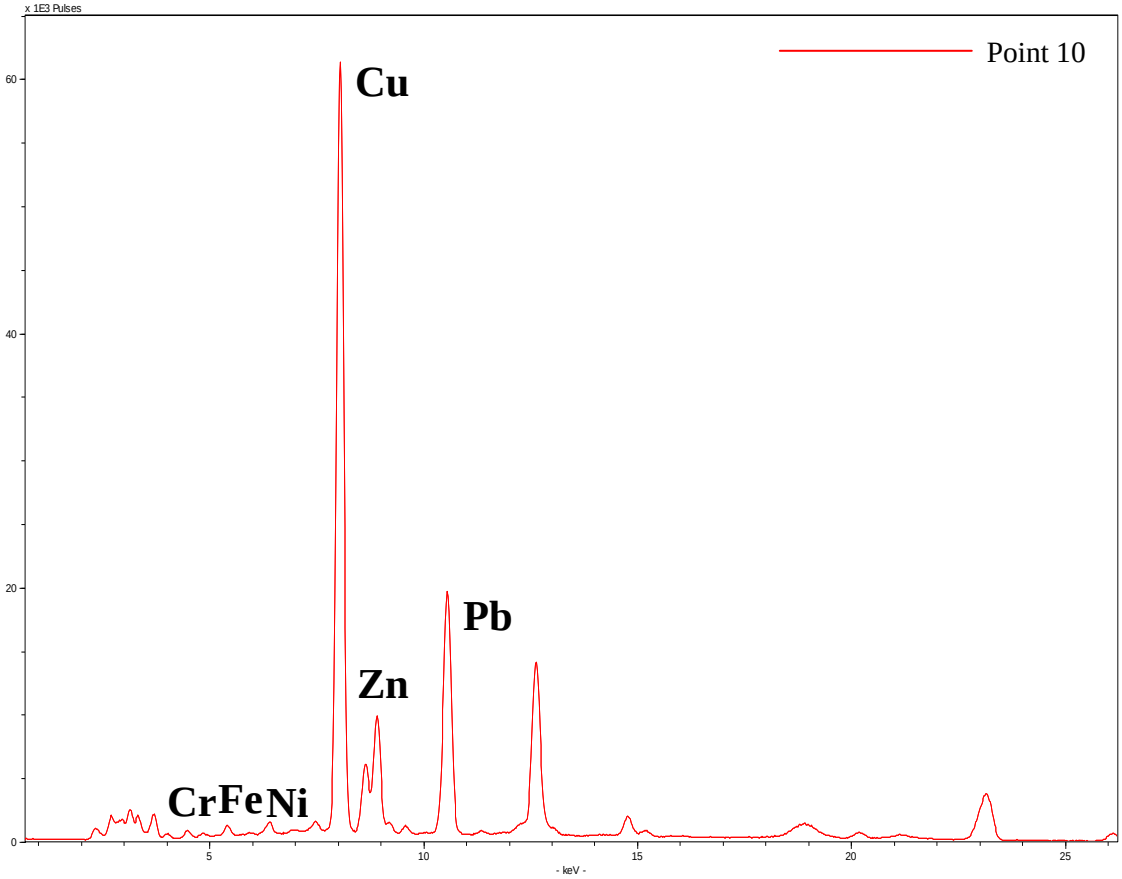

Figure 9. *Sunset November 1899*. Point eight, green.

Signature

The two largest peaks for the signature, point 10, are copper and lead (figure 10). This is representative of the background, and without any peaks that really stand out for the signature, it is either a blend of several paints or an organic-based black pigment like carbon black.

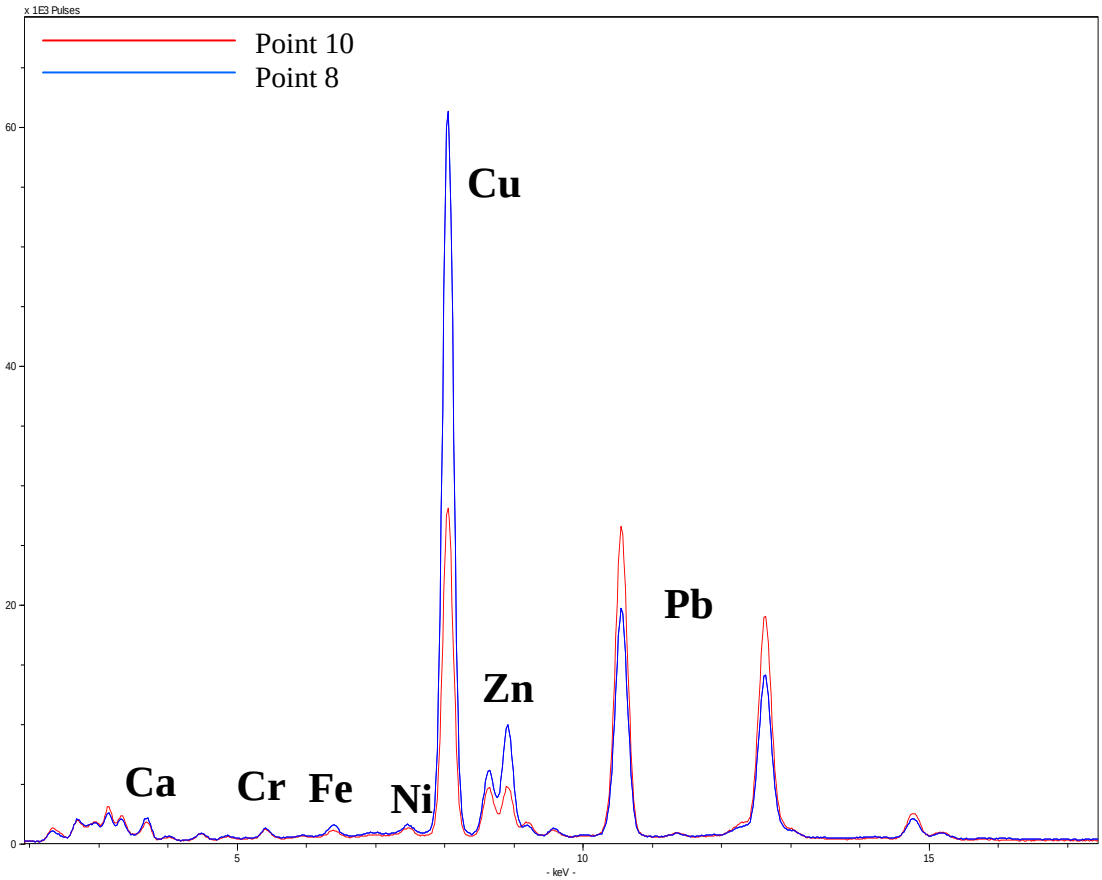

Figure 10. *Sunset November 1899*. Point 10, the signature, compared to point 8, the green.

Sand Dunes

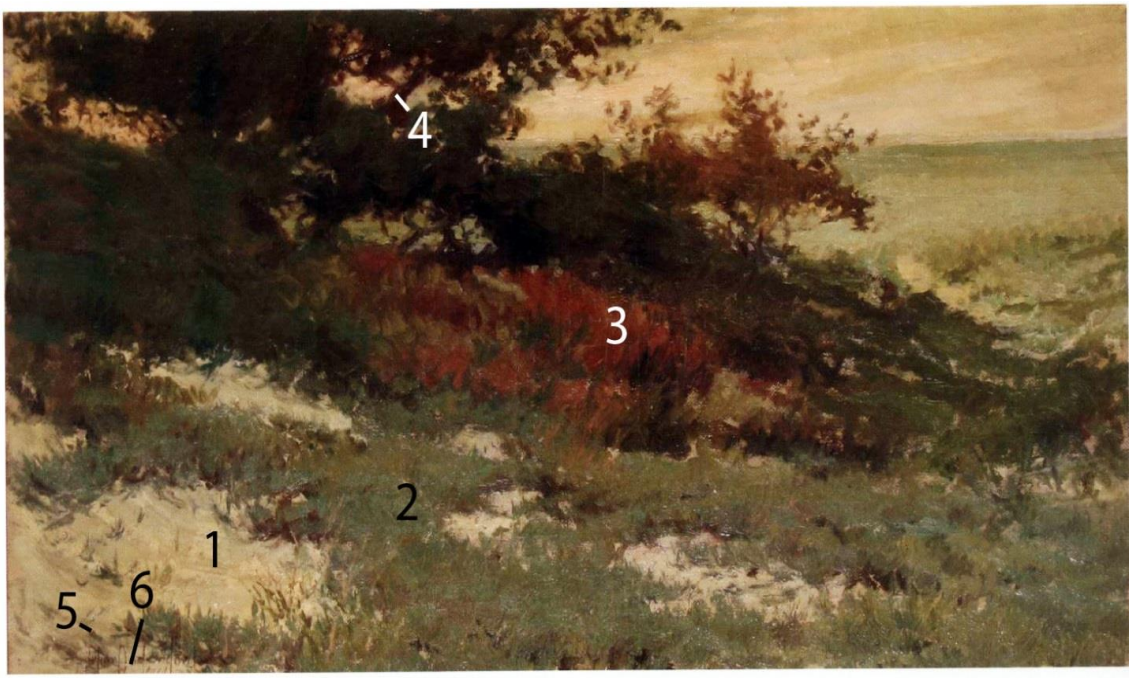

Figure 11. *Sand Dunes*, 1901, oil on canvas, signed Julian Onderdonk, 16in x 30in, from Villa Finale, San Antonio, TX.

A total of six points were analyzed for *Sand Dunes* (figure 11). Point 1 is the beige color of the dirt, point 2 is the green of the grass, point 3 is the red leaves, point 4 is the darkest green in the trees, close to black, point 5 is the background for the signature, and point 6 is the signature. There is a strong peak for lead in each reading, indicating that this painting has a lead based primer.

White

Points 1 and 5 are primarily a beige color, with point 5 having some darker streaks in it as well. Both spectra are very similar, with the exception of zinc; point 5 has a distinct peak, while point 1 does not (figure 12). Point 5 also has higher peaks for zinc, chromium, and barium, which suggests that these are all elements present in the darker pigment, not the lighter. This may be a lead white with iron red, zinc yellow, and copper green.

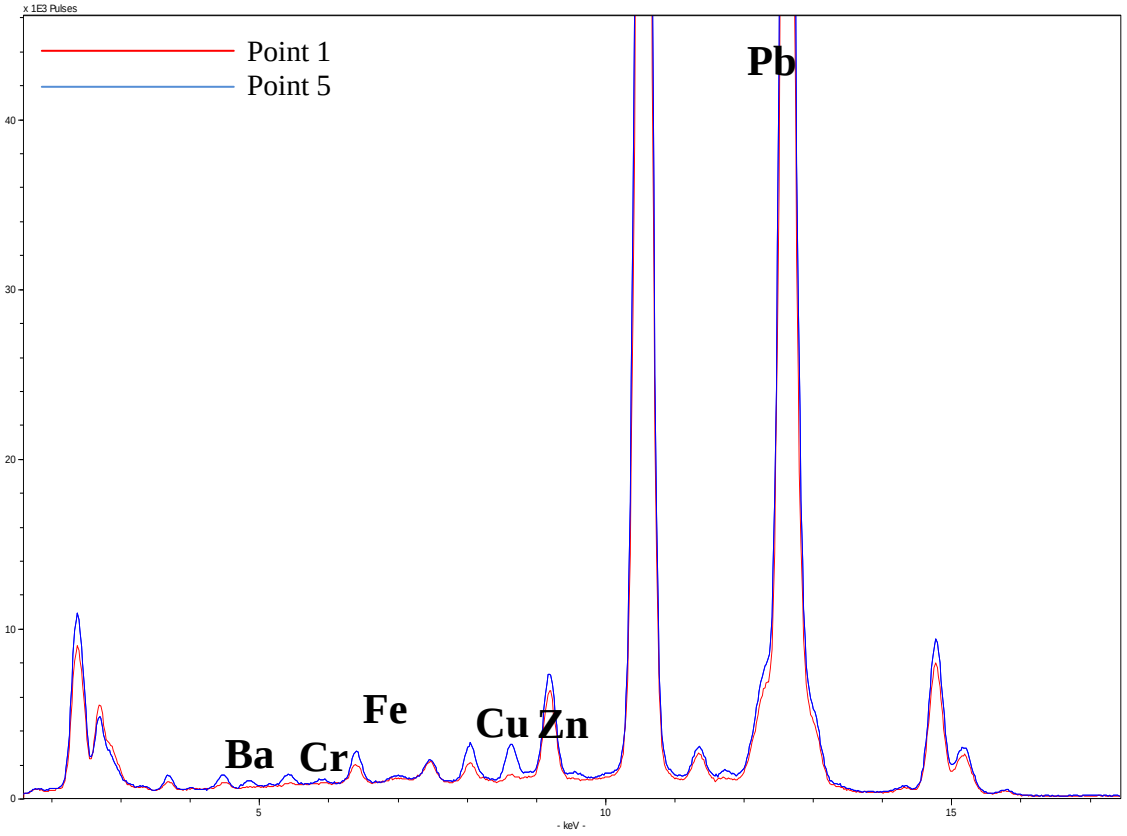

Figure 12. *Sand Dunes* Points 1 and 5, the whites.

Green and Red

The two greens, points 2 and 4 are very similar, though the lighter green, point 2, has a higher level of lead (figure 13). A higher lead peak is likely indicative of a thinner paint surface or more white under paint, and is not part of the green pigment. The green is pigment is a mixture of chromium oxide green and a copper based green such as malachite or verdigris. The darker green, being mixed with other paints to achieve the dark color, lends insight to the other pigments being used as well. The peak of barium indicates the use of barium yellow, while the peak of iron indicates a hematite based red. This, combined with the elevated zinc peak, might point to a blended green like zinc chrome green, which is a blend of zinc chromate yellow and Prussian blue, an iron based blue. The dark green also has a distinct peak for arsenic, which it shares with point 3, red, but not point 1 or 2. This points to realgar, an arsenic based red.

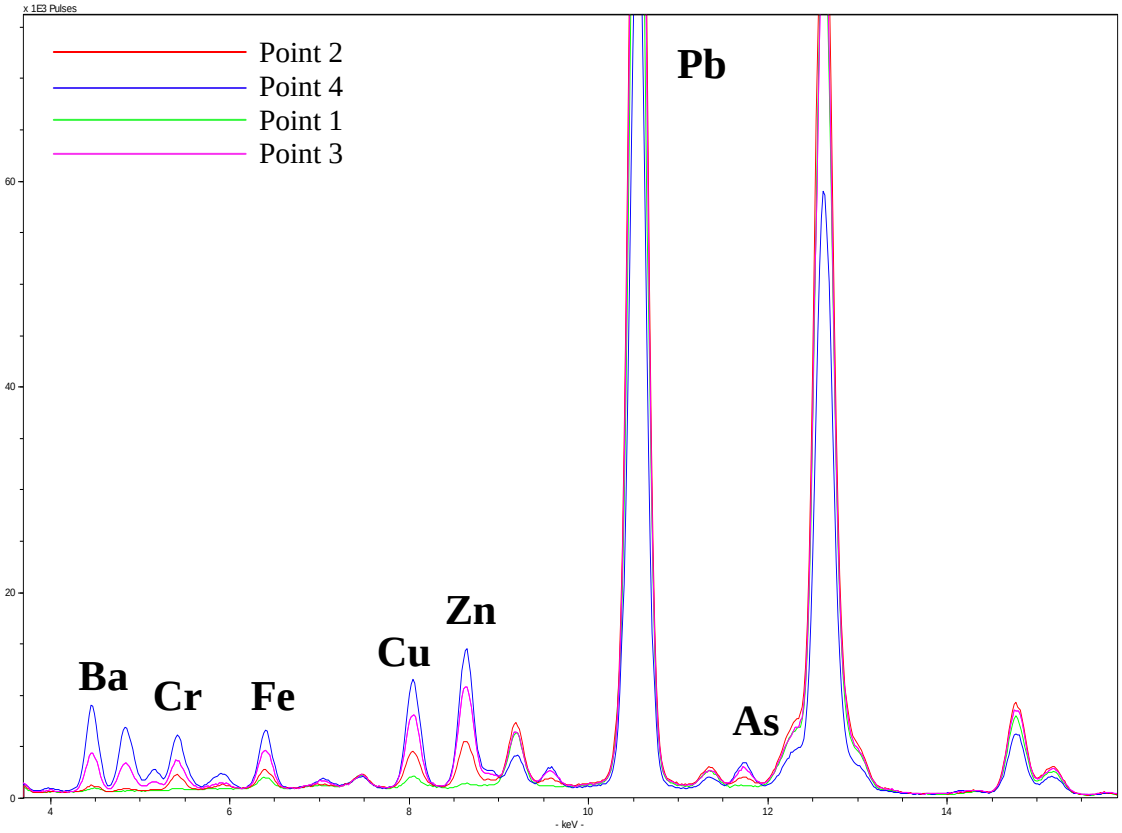

Figure 13. *Sand Dunes* Points 2 and 4, the greens, compared to points 3, the red, and point 1, white.

Signature

Unlike the dark green of the tree trunk in point 2, the signature appears to be a mixture of iron, zinc, and copper based pigments, indicating a blend of hematite based red and the copper based verdigris green (figure 14). The zinc peak again likely points to zinc chrome green, which is a blend of zinc chromate yellow and Prussian blue.

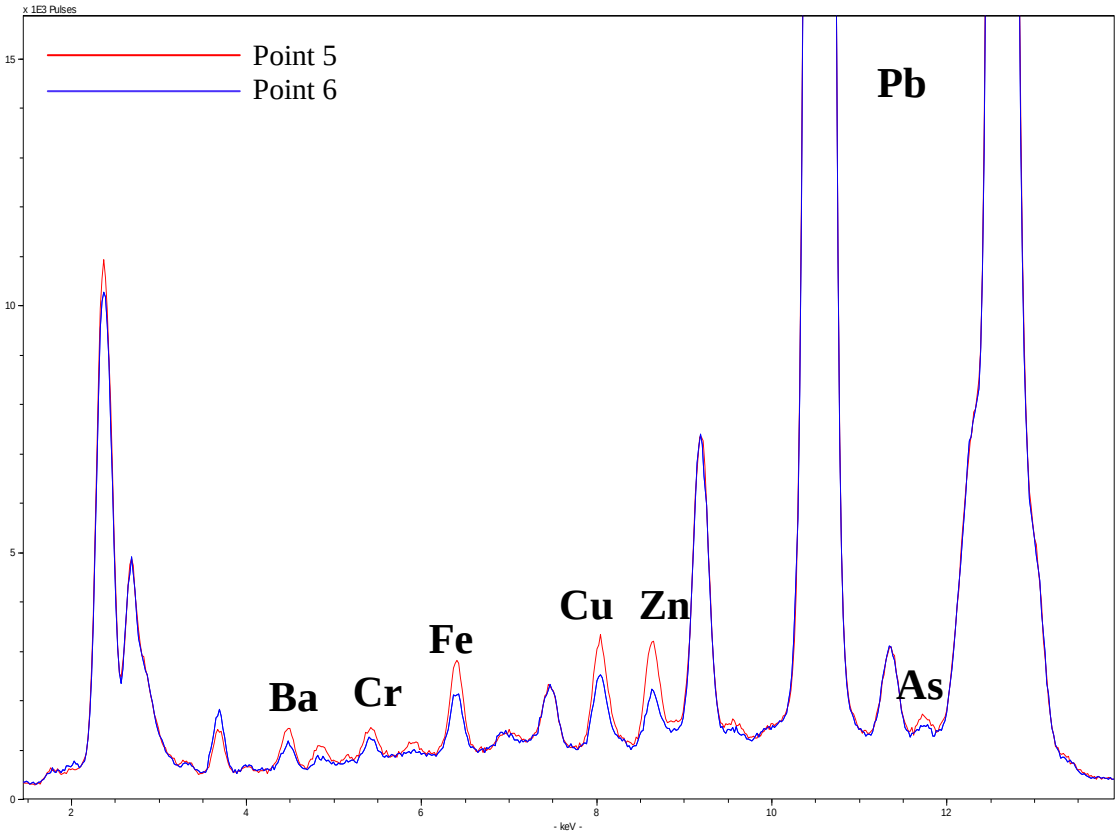

Figure 14. *Sand Dunes* Point 5, the background and point 6, the signature.

Cock Fight Amid the Jacals

Figure 15. *Cock Fight Amid the Jacals*: 1905, oil on Canvas, signed Chas Turner, 12in x 20in, from the James and Kimel Baker Collection, College Station, TX.

For *Cock Fight Amid the Jacals* (figure 15), fourteen points were taken, including the primer. Point 1 is the white in the cloud, point 2 is the blue of the sky, point 3 and 4 are whites from the shirts, point 5 and 6 are reds from the clothes, point 7 is the yellow of the house, point 8 is the yellow brown of the hill, point 9 and 10 are the brown roofs, point 11 is the white wagon cover, point 12 is the green of the grass, point 13 is the green of a tree, and point 14 is the primer.

White

Points 1, 3, and 4 are white, and point 11 is the grayish white of the covered wagon. All of the white pigments on the painting are overwhelmingly lead based, and, like the majority of the paintings signed by Onderdonk or Turner, this white is a pigment derived from carbonate of lead (figure 16). Lead whites have been in use since antiquity, so as for the authenticity of the painting, there is no problem with the availability. The whites also have trace amounts of tin, cadmium, zirconium, zinc, copper, iron, nickel, manganese, chromium, and titanium, though only iron and zinc are present in appreciable quantities. In points 3 and 4, the purest samples of white on the painting, there is a higher level of iron and mercury present, but given the proximity to the red scarves above them, it seems likely that these result from the red pigment there.

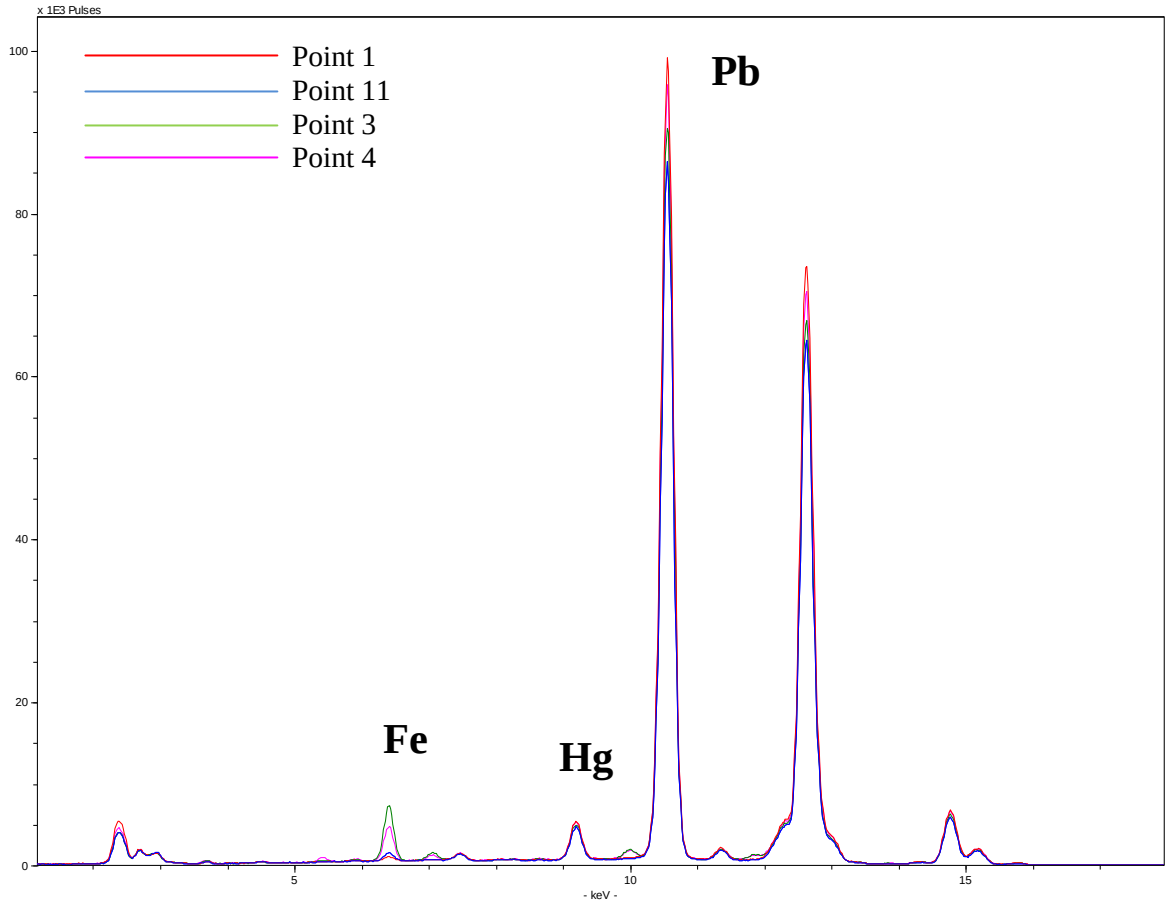

Figure 16. *Cock Fight Amid the Jacals*: Points 1, 3, and 4, whites, and point 11, grey.

Blue

Point 2 is taken from the blue pigment in the sky. Unfortunately, the blue spectra is indistinguishable from point 1, the white in the sky (figure 17). Compared to points 3 and 4, the iron content is significantly less in point 2, but this is again likely due to spill over from the red so close to points 3 and 4. Comparing point 2 to point 11, the grayish white, there is again a lower energy signature for the iron, this time without fear of interference (figure 18). The lower level of iron precludes the use of aerinite or Prussian blue ($Fe_4[Fe(CN)_6]_3$)., and the fact that there is no significant presence of copper, sulfur, aluminum, cobalt, or bromine over the white pigments precludes the use of ultramarine, azurite, cobalt blue, Egyptian blue, smalt, or Tyrian purple. Given the data, the most likely explanation is that the blue used is an organic pigment like indigo ($C_{16}H_{10}N_2O_2$), which is undetectable via the Bruker XRF (Artioli 2010, 269; Douma 2008).

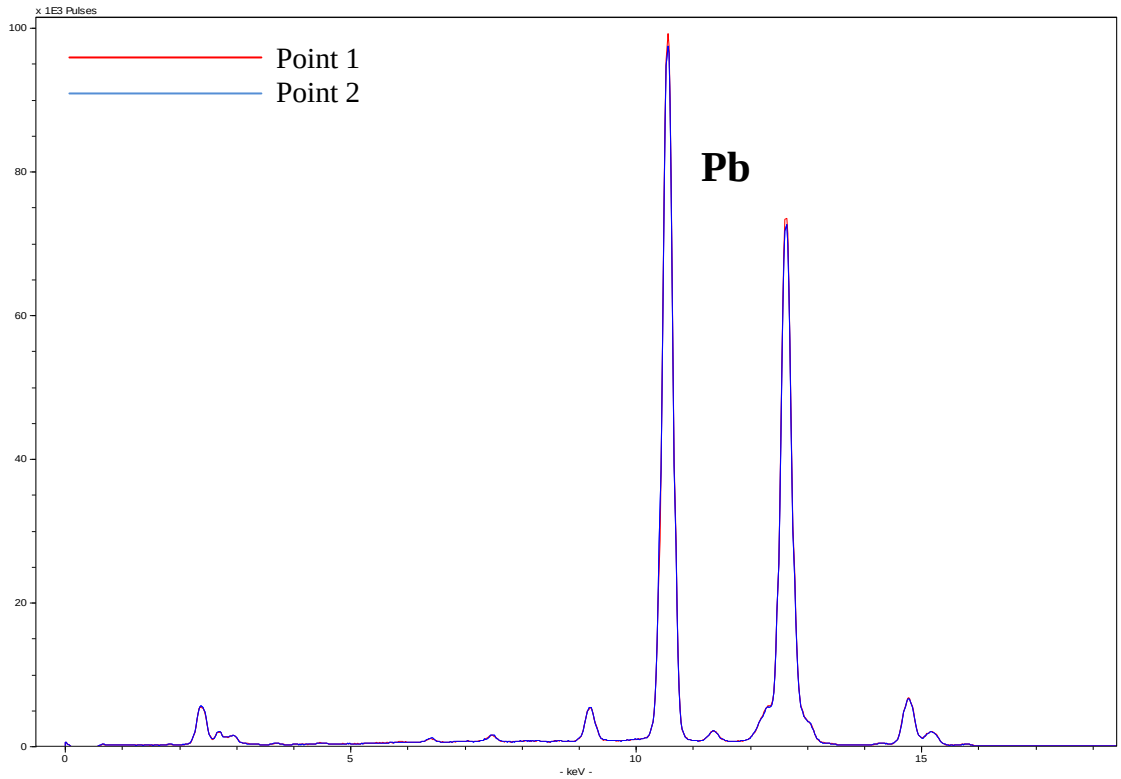

Figure 17. *Cock Fight Amid the Jacal*, Point 2, blue, compared to point 1, white.

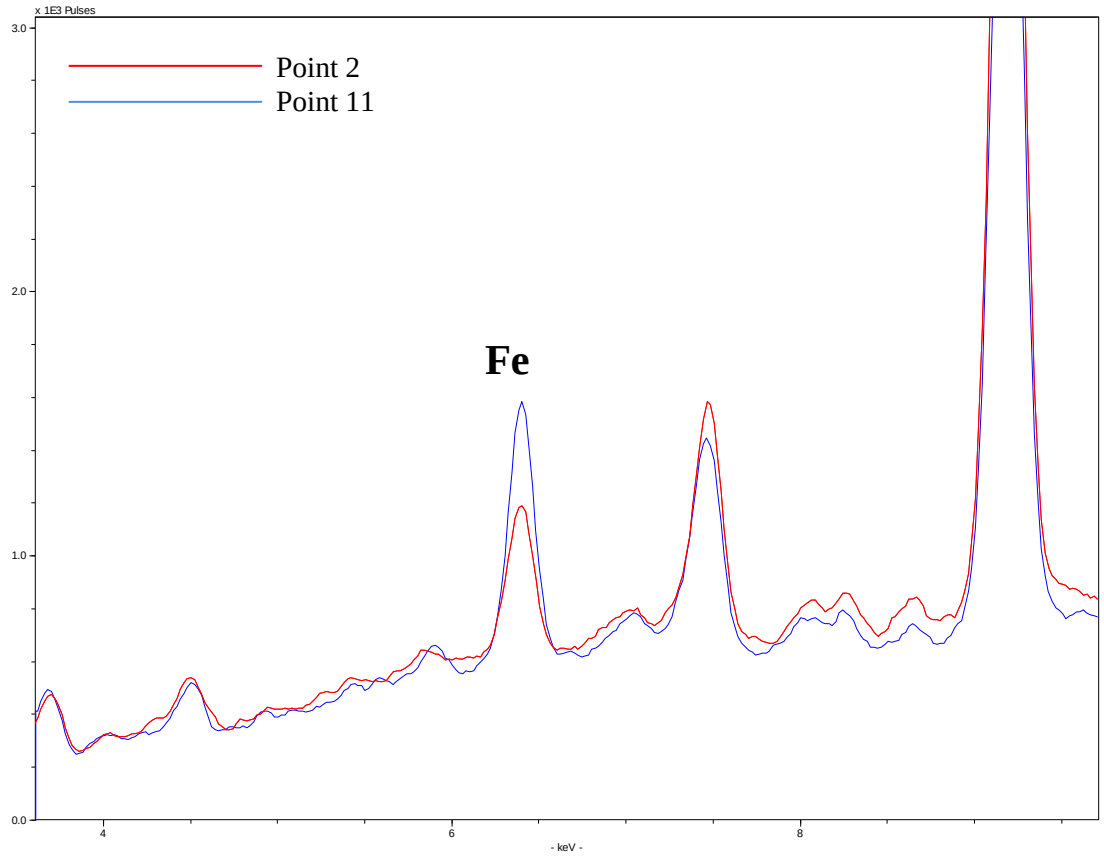

Figure 18. *Cock Fight Amid the Jacals*, Point 2, blue, compared to point 11, gray.

Red

The red points 5 and 6 were taken from the clothing of two of the individuals depicted. Iron and lead levels are consistent with the white in points 3 and 4, but there is an even more elevated mercury signal (figure 19). This is very likely indicative of realgar (HgS).

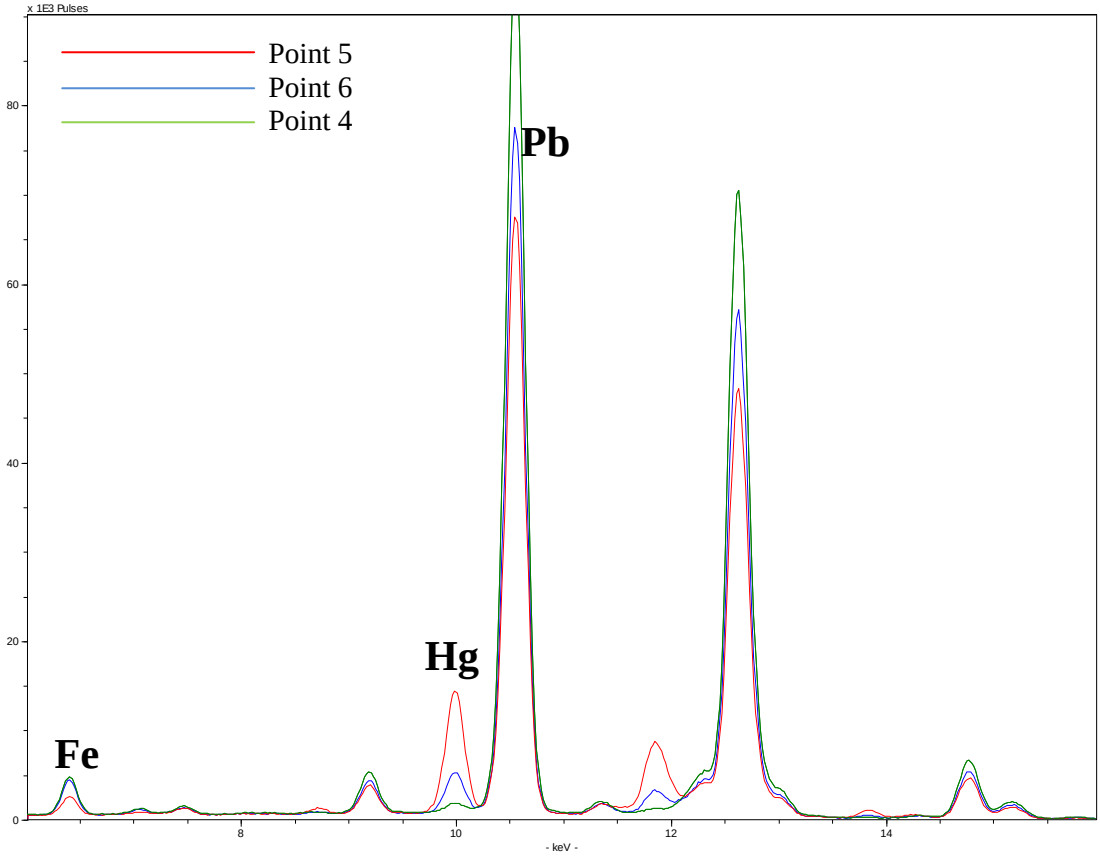

Figure 19. *Cock Fight Amid the Jacals*, Points 5 and 6, the reds, compared to point 4, white.

Yellow

The yellows, taken from the side of the house, point 7, and the side of the hill, point 8, have a strong lead component and the addition of tin (figure 20), indicating a possible use of lead-tin yellow, though this is unlikely due to the fact that it fell out of use after the turn of the 18th century. There are also trace amounts of strontium and chromium, which can indicate the presence of lemon yellow ($SrCrO_4$). However, when compared to the white of the sky, the most obvious difference is that the yellow pigments have an elevated level of iron. This means the most likely yellow pigment being used was a yellow ochre, also known as limonite (FeO(OH)).

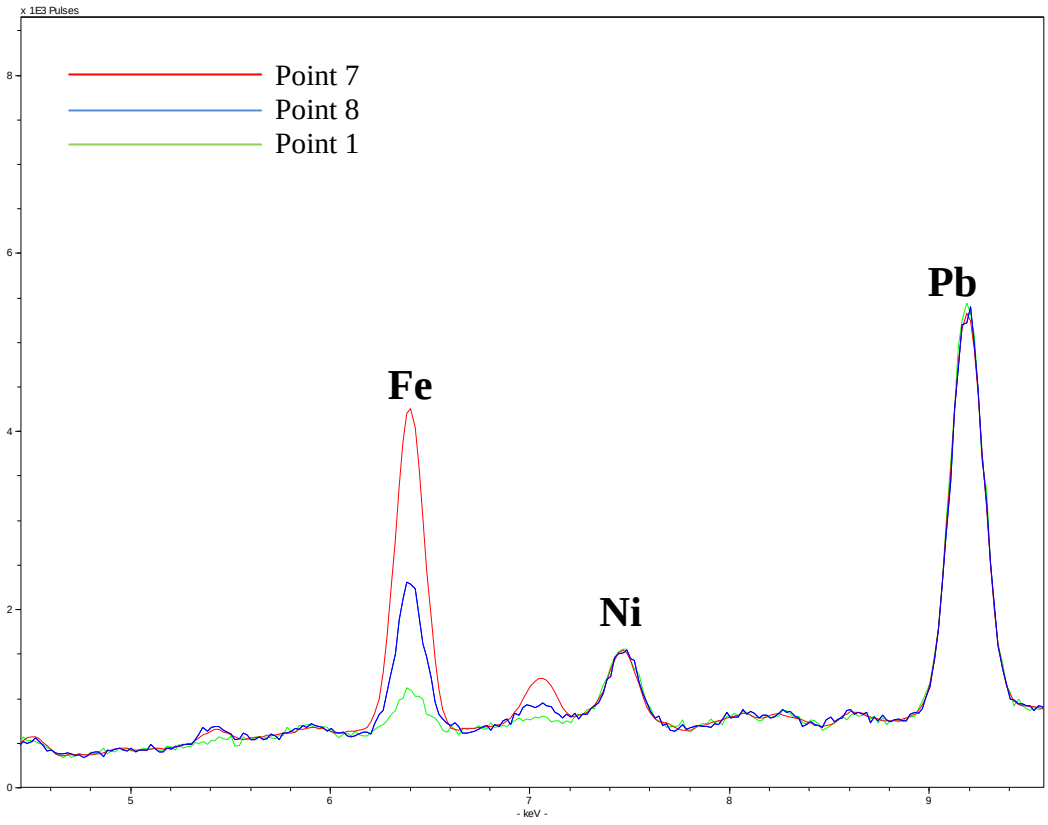

Figure 20. *Cock Fight Amid the Jacals*, Points 7 and 8, yellows, compared to point 1, white.

Brown

Points 9 and 10 are taken from the brown roofs at the right of the painting. The spectra for the brown points are very similar to the yellow, which suggests that the primary color in the brown blend is the ochre mentioned above (figure 21). There is no mercury present, which precludes the red from being present, and without magnesium present, it is unlikely that it is Van Dyke brown (Fe_2O_3 (· H_2O) + MnO_2·(n H_2O) + humic acids) or Umber (Fe_2O_3 (· H_2O) + MnO_2·(n H_2O)+ Al_2O_3). Therefore, the browns are most likely a blend of the limonite yellow and another color, or an organic based pigment.

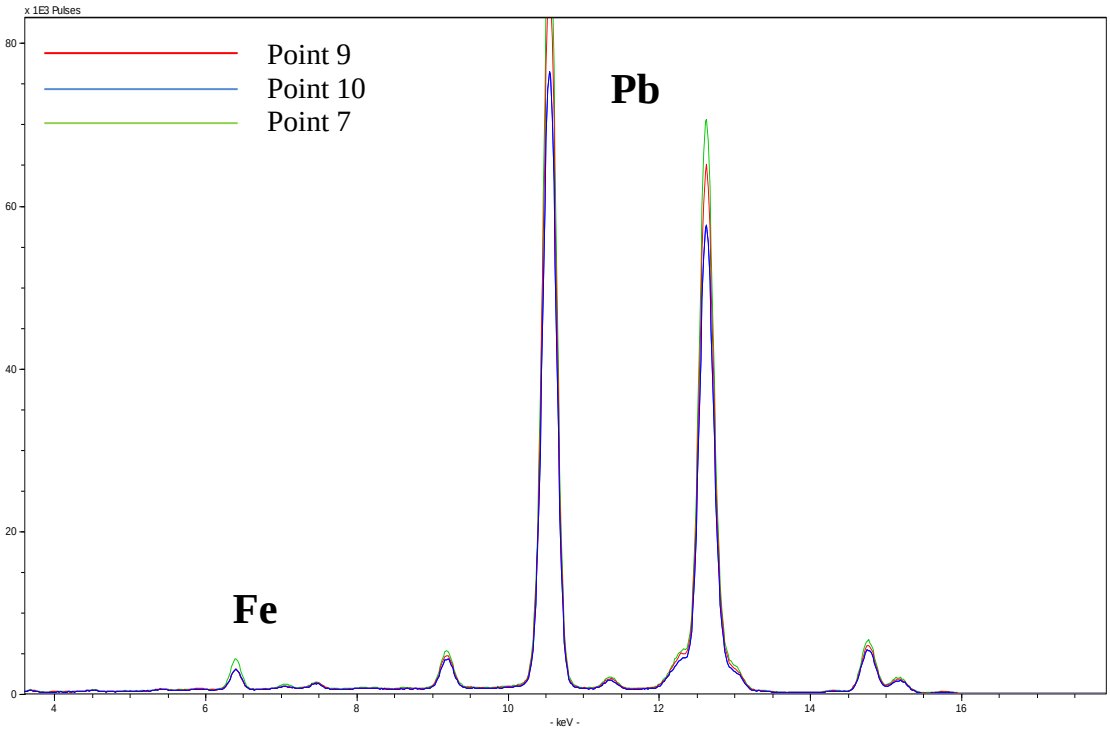

Figure 21. *Cock Fight Amid the Jacals*, Points 9 and 10, brown, compared to point 7, yellow.

Green

The spectra for points 12 and 13, greens taken from the grass and a tree respectively, show elevated levels of chromium over the rest of the pigments analyzed in this painting, likely pointing to the use of viridian green, a chromium oxide dehydrate ($Cr_2O_3 \cdot 2\ H_2O$). The only other pigment analyzed on the painting that comes close in chromium levels is the white from point 4, taken from the shirt of the man in the middle of the painting. Figure 22 shows points 12 and 13 overlaid with all of the other spectra to emphasize the relative levels of chromium in the non-green areas of the painting.

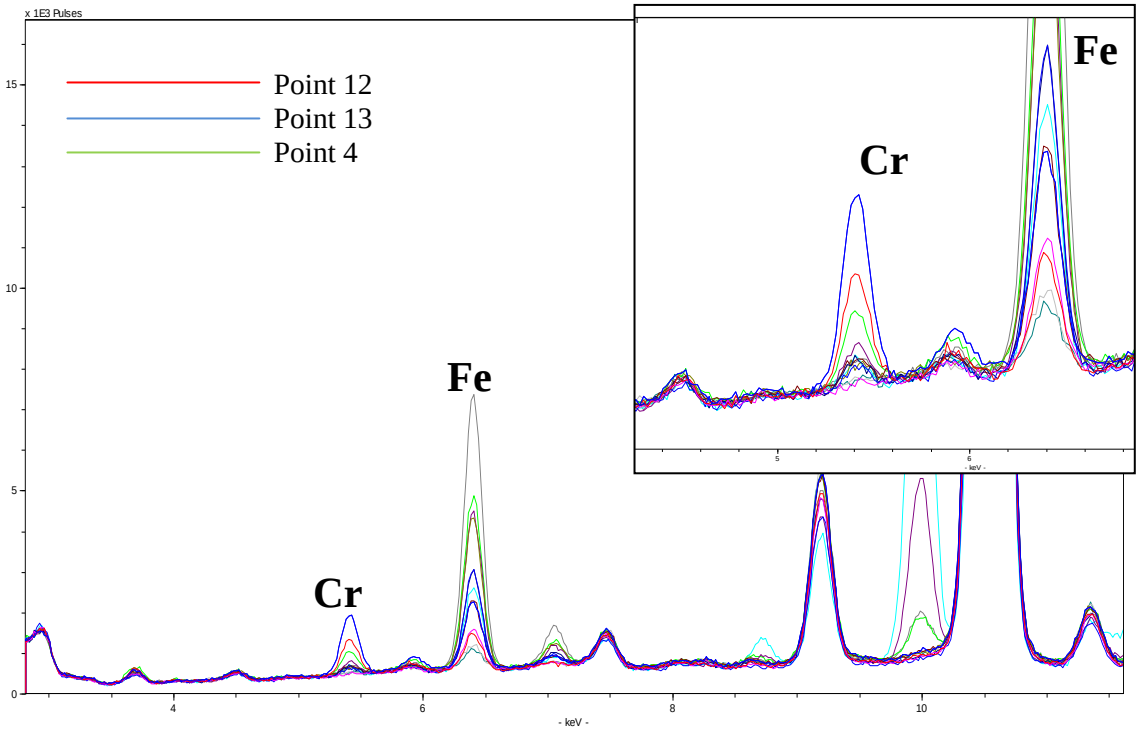

Figure 22. *Cock Fight Amid the Jacals*, Points 12 and 13, compared to all spectra from this painting.

Primer

Point 14, the primer, was taken from the side of the canvas that had not been painted over with anything but the primer. Unfortunately, the nails used to tack the painting to its auxiliary frame were corroded, and had spilled far too much iron into the canvas to come to any definitive pigment used for the primer. If the iron is discounted as contamination, the primer looks very similar to point 1, the white that had the least amount of mercury interference from the nearby red (figure 23). This suggests a lead white primer was used.

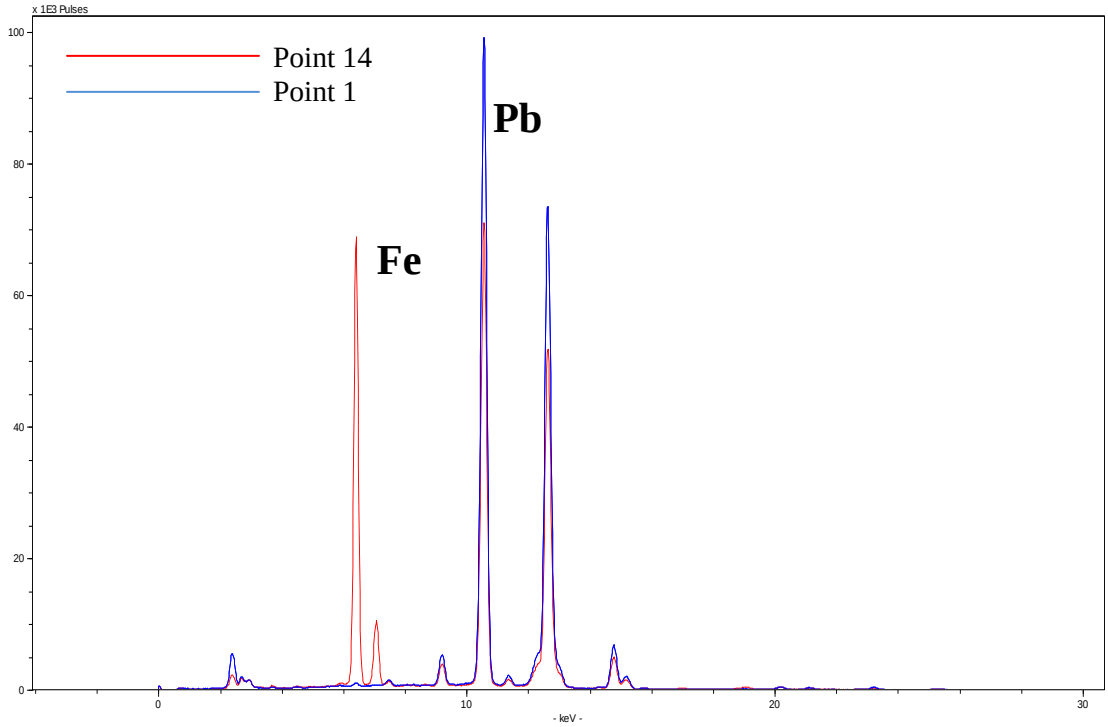

Figure 23. *Cock Fight Amid the Jacals*, Point 14, the primer, compared to point 1, white. Note the high level of iron from the corrosion of the nail.

Portrait of G. Beddle Moore

Figure 24. *Portrait of G. Beddle Moore*: 1905, Signed Julian Onderdonk, Oil on Canvas, 9.9in x 7.5in, Witte Museum, San Antonio, TX.

A total of five points were analyzed for *Portrait of G. Beddle Moore* (figure 24). Point 1 is the light skin tone of the forehead, point 2 is the white of the collar, point 3 is the white of the shirt, point 4 is the black of the jacket, and point 5 is the darker skin tone of the cheek.

White

The white points 2 and 3 have the expected peaks of the lead white primer, and then show peaks for zinc and barium (figure 25). The zinc is likely zinc white, while the barium could be either barium white or barium yellow.

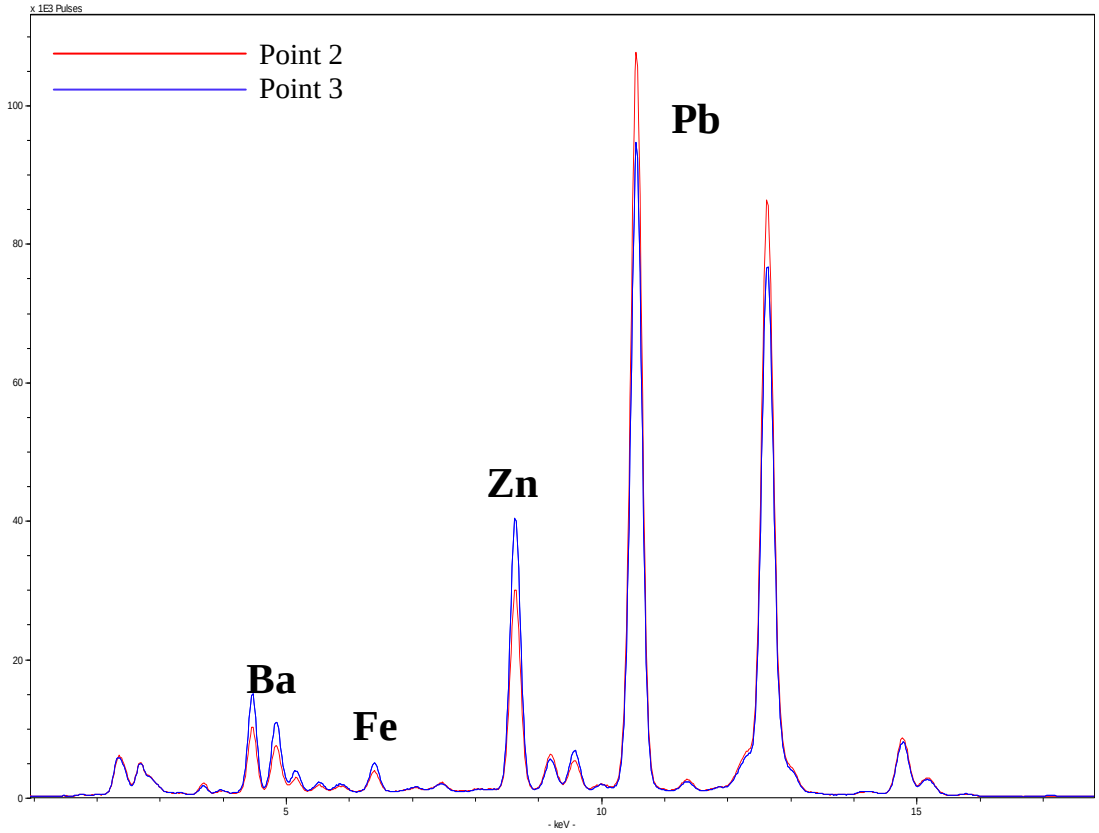

Figure 25. *Portrait of G. Beddle Moore*, Points 2 and 3, the whites.

Skin Tones

Point 1, the lighter skin tone, is similar to that of the whites of point 2 and 3 with the exception of mercury, likely realgar red. Given this, it is likely that either the zinc or the barium seen in the white points is a yellow. Without a more diverse range of hues in this painting, they are both candidates for either color. The darker skin tone of point 5 maintains the mercury of point 1, but there is a strong iron spike as well, indicating an ochre for a more earth-toned red or brown (figure 26).

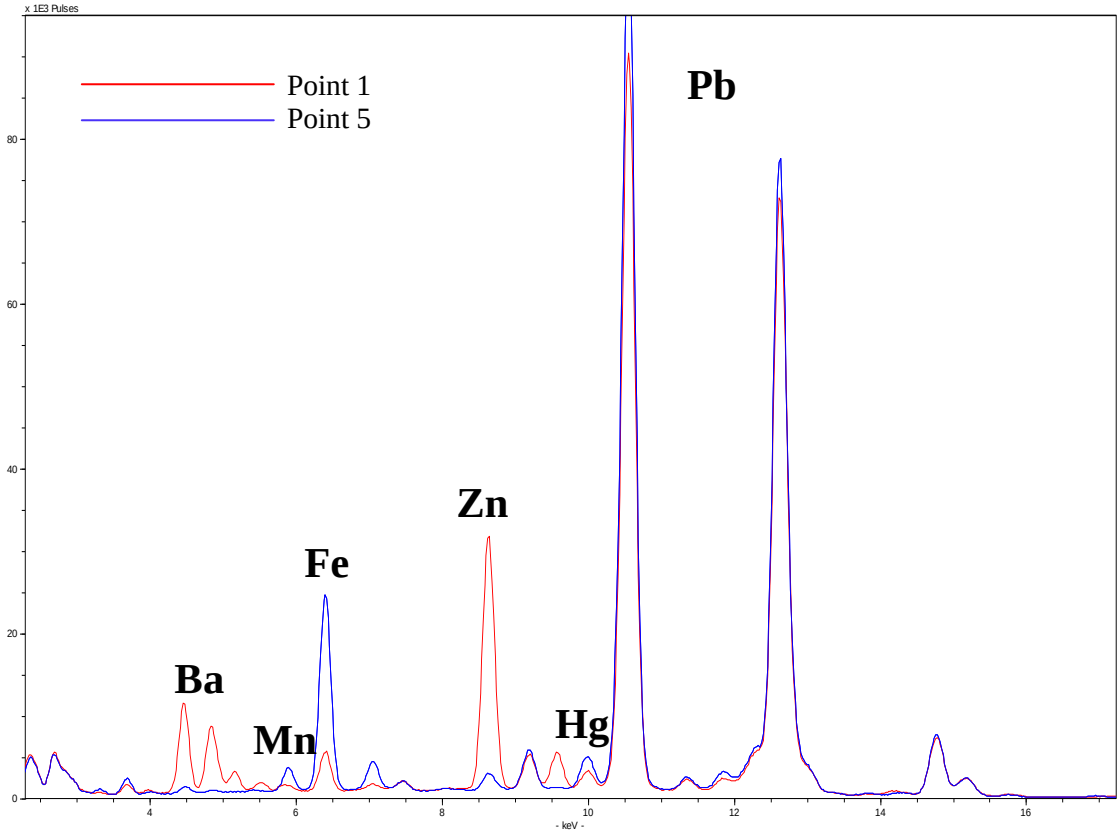

Figure 26. *Portrait of G. Beddle Moore*, Points 1 and 5, red and yellow skin tones.

Black

The black of the jacket, point 4, lacks the iron and mercury of the dark skin tone, but does have a strong calcium peak (figure 27). This likely indicates the use of a carbon-based black pigment like bone black, which is made by charring animal bones. The carbon produced from the charring process also contains the calcium from the bones (Wehlte 1975, 165), leaving calcium as a signature for this pigment despite the inability to detect C with the pXRF. There is also a peak for manganese, which likely indicates manganese black or manganese brown, both terms interchangeably used for Mn_2O_3, known since the late 19th century (Eastaugh et al. 2008, 255).

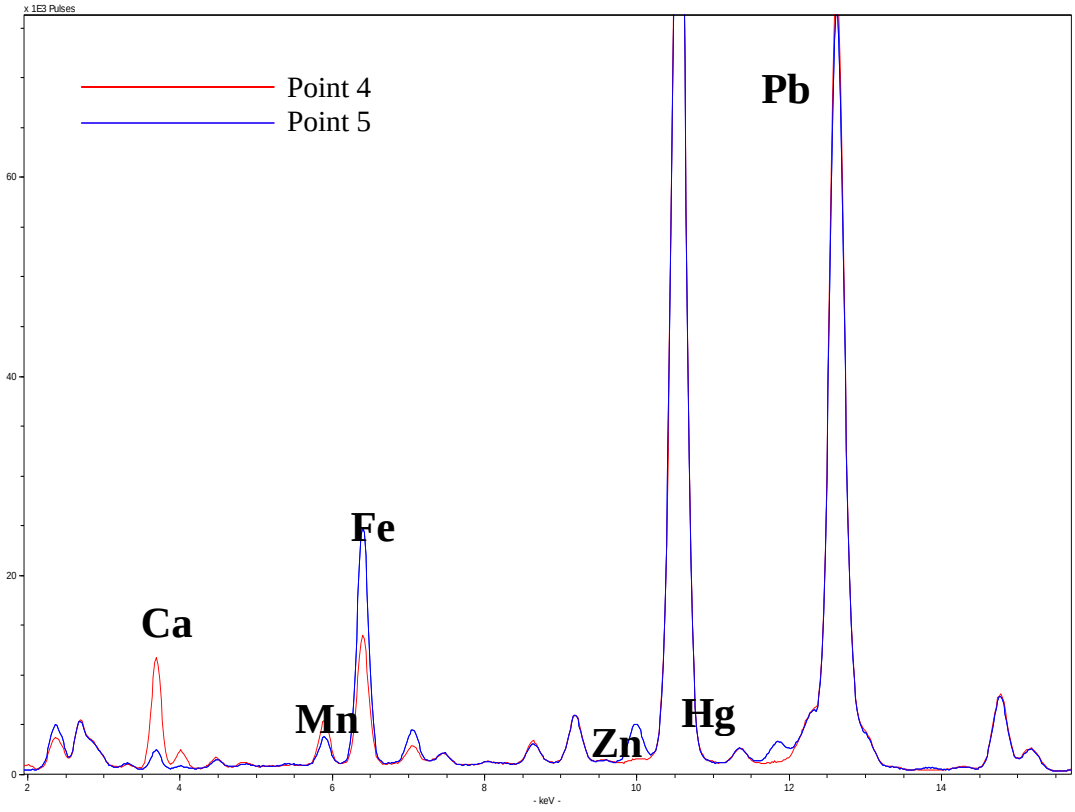

Figure 27. *Portrait of G. Beddle Moore*, Points 1, black compared to the skin tone of point 5.

Harbor Scene

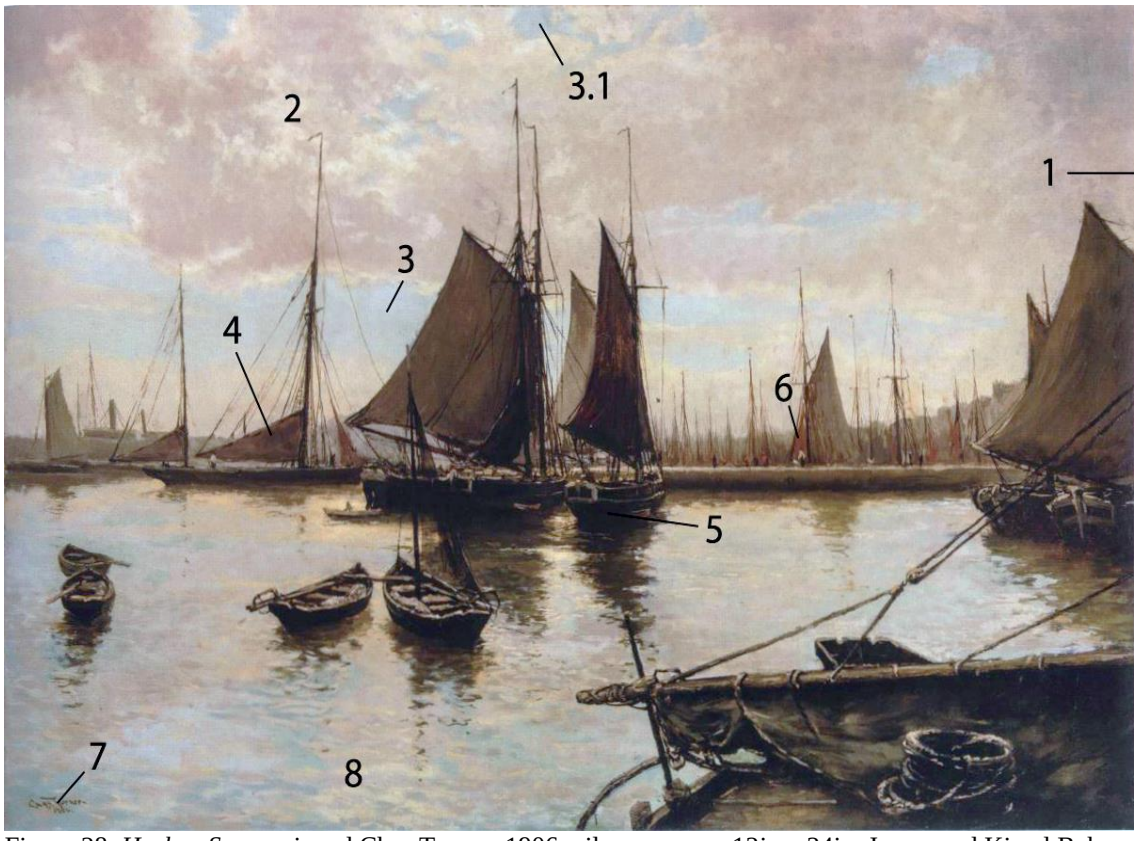

Figure 28. *Harbor Scene*, signed Chas Turner, 1906, oil on canvas , 12in x 24in, James and Kimel Baker Collection, College Station, TX.

For *Harbor Scene* (figure 28), a total of nine points were analyzed, including a section of the primer without paint on it examined while the painting was out of its frame. Point 1 is the primer, point 2 is the white of the sky, points 3 and 3.1 are the blues of the sky, points 4, 5, and 6 are various hues of reddish ochre, point 7 is the signature, and point 8 is blue and white of the water.

White and Blue

Comparing point 1, the primer, to point 2, the white of the cloud, the only discernable difference between the two points is the higher level of calcium in point 2 (figure 29). This could indicate that a chalk white was used, or that ivory or bone black was the source of the gray surrounding the white. Points 3, 3.1, and 8, all variations of a white and blue mixture, are similar in composition to the white and primer (figure 30). Point 8, the water, has a higher peak for iron, indicating that the blues are a Prussian blue, which is iron based.

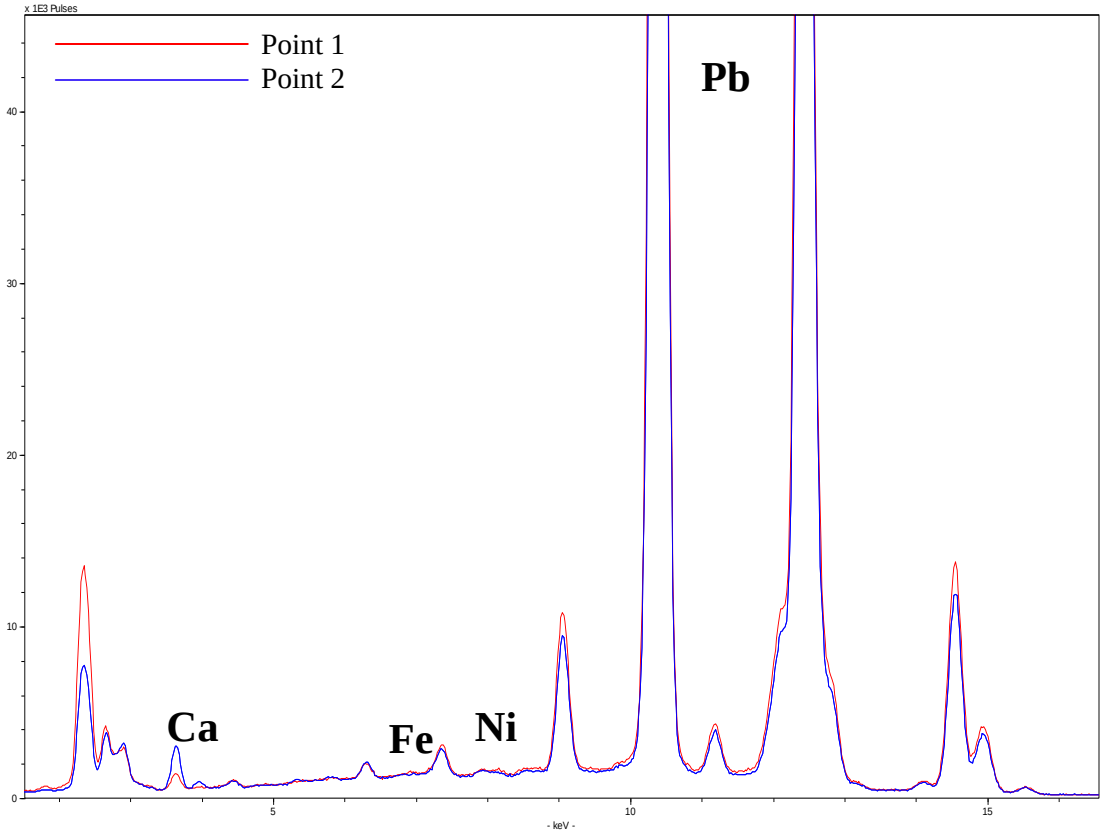

Figure 29. *Harbor Scene*: Point 1, the primer, compared to point 2, the white of the cloud.

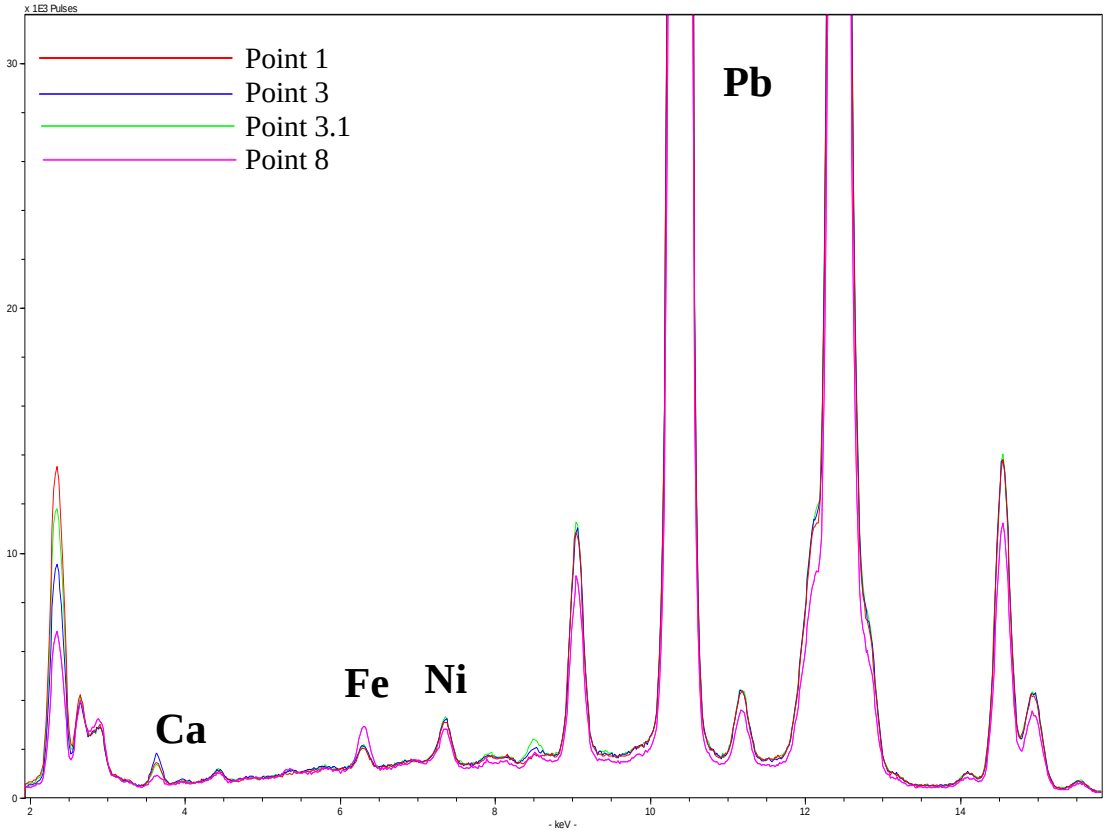

Figure 30. *Harbor Scene*, Point 1, the primer, compared to point 3 and 3.1 and 8, all blue and white.

Brown and Red

Point 5, the brown from the hull of the ship, is distinctly iron based, which would be a hue of ochre. Point 6 on the other hand, having almost no iron, is vermillion, an Hg based red. Point 7, the signature, is similar in composition to the hull, an iron based ochre brown (figure 31).

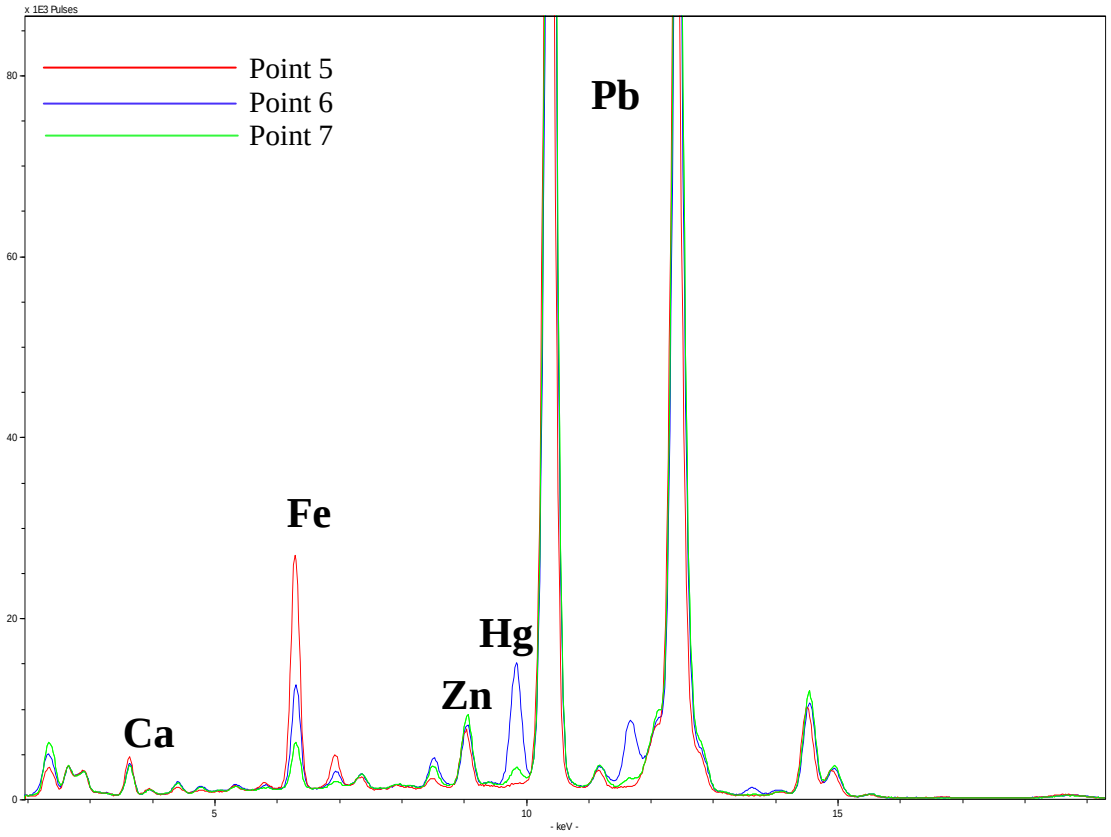

Figure 31. *Harbor Scene*, Point 5, 6, and 7, browns and reds.

October Sullivan Co, NY

Figure 32. *October, Sullivan Co. NY*. 1908, Signed Julian Onderdonk. Oil on Board, 6in x 9in, James and Kimel Baker Collection, College Station, TX.

For *October Sullivan Co, NY* (figure 32), six points were analyzed. Points 1 and 2 are whites from the sky, points 3 and 4 are blues from the sky, point 5 is the green of the grass in the center left of the painting, and point 6 is the signature.

White

Points 1 and 2, as seen below in figure 33, show the typical spectra for lead white. Zinc, nickel, iron, chromium, titanium, and calcium are also present, but it is an overwhelmingly lead based white in both points.

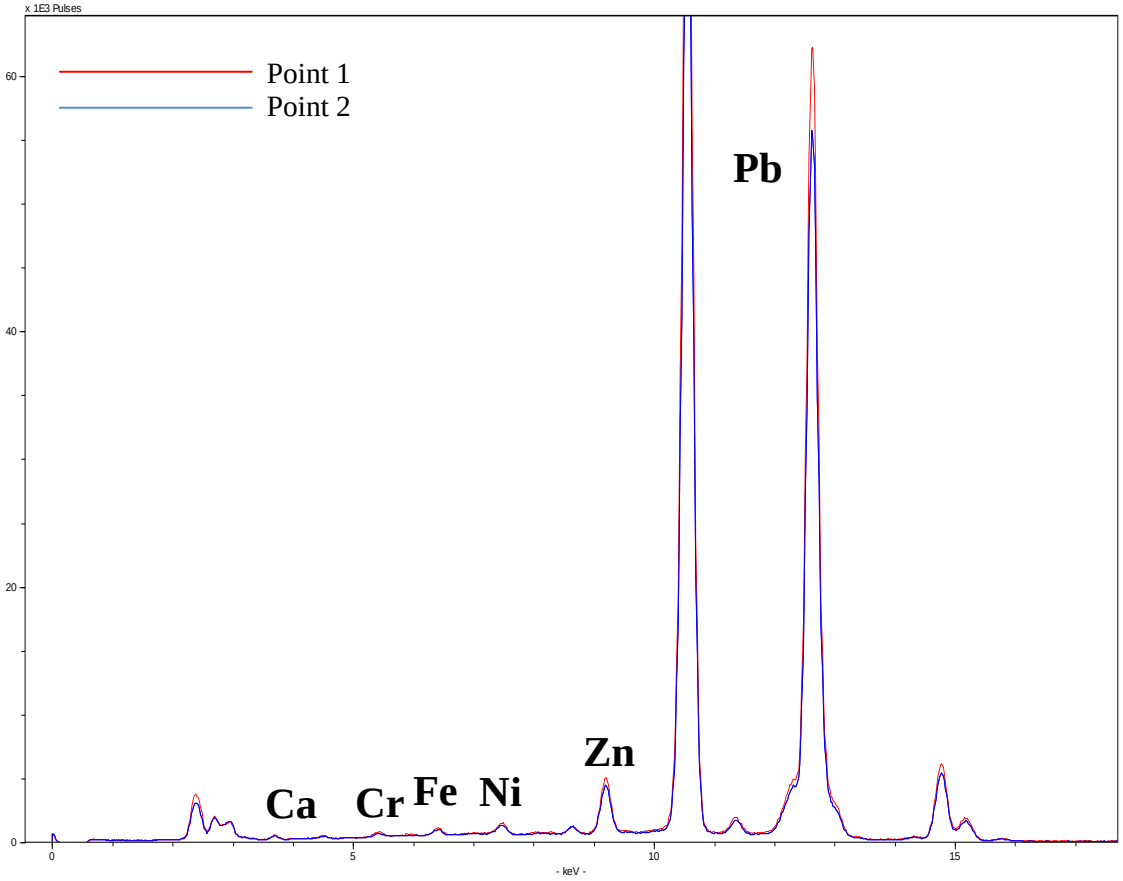

Figure 33. *October, Sullivan Co. NY.* Points 1 and 2, the whites.

Blue

The only element the blue points 3 and 4 have over the white pigment in points 1 and 2 is zinc (figure 34). Zinc is not used for the manufacture of blue pigment, so the zinc is either another shade of white, which is unlikely given the lower value in the actual white, or from something else. In this case, looking carefully at the blue, it is likely from zinc yellow (ZnCrO4). This accounts for the zinc and the chromium, and means that the blue is either Prussian blue, or organic in nature, like indigo.

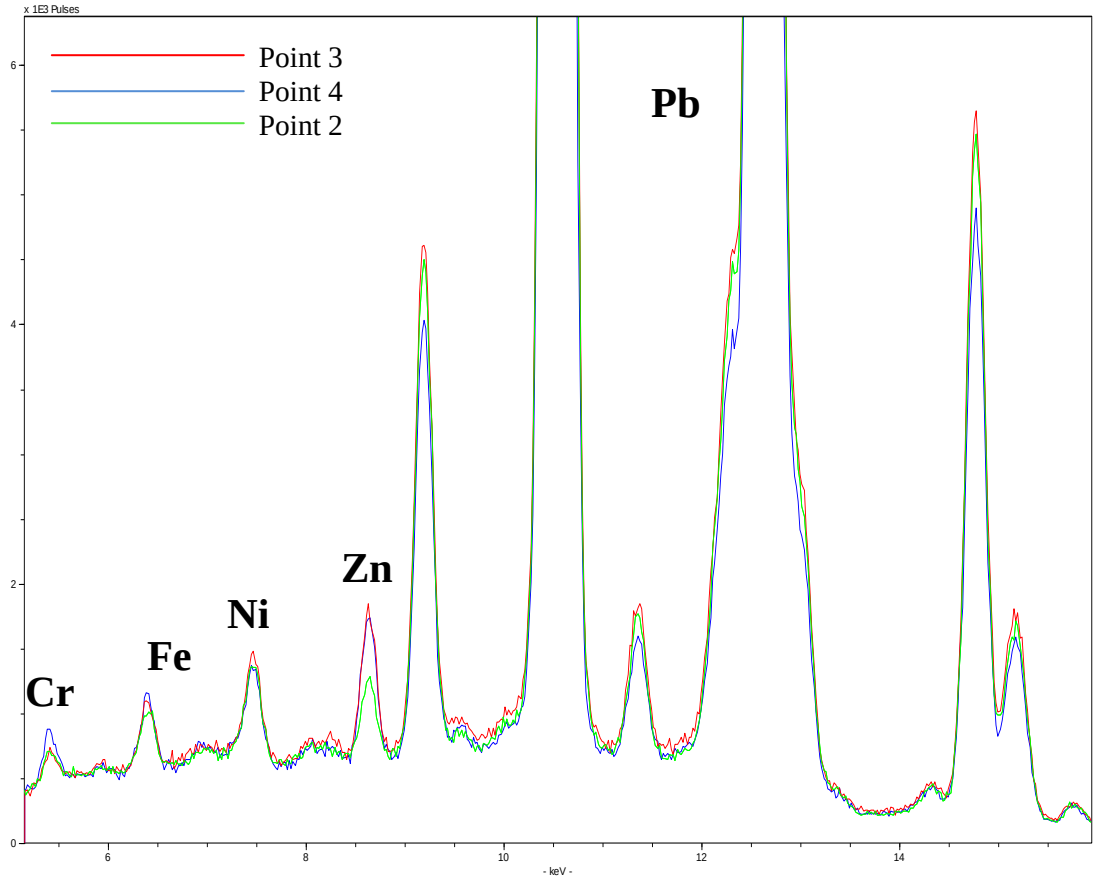

Figure 34. *October, Sullivan Co. NY.* Points 3 and 4, the blues, compared to point 2, white.

Green

Point 5, the green of the grass in the foreground, is made up of barium, chromium, iron, and zinc (figure 35). The barium and some of the chromium are likely from lemon yellow, the zinc, as mentioned above is likely zinc yellow, the iron is likely accounted for by the reddish tint beneath the green, ochre, and the green then therefore must be from chromium oxide, or viridian (Cr2O3).

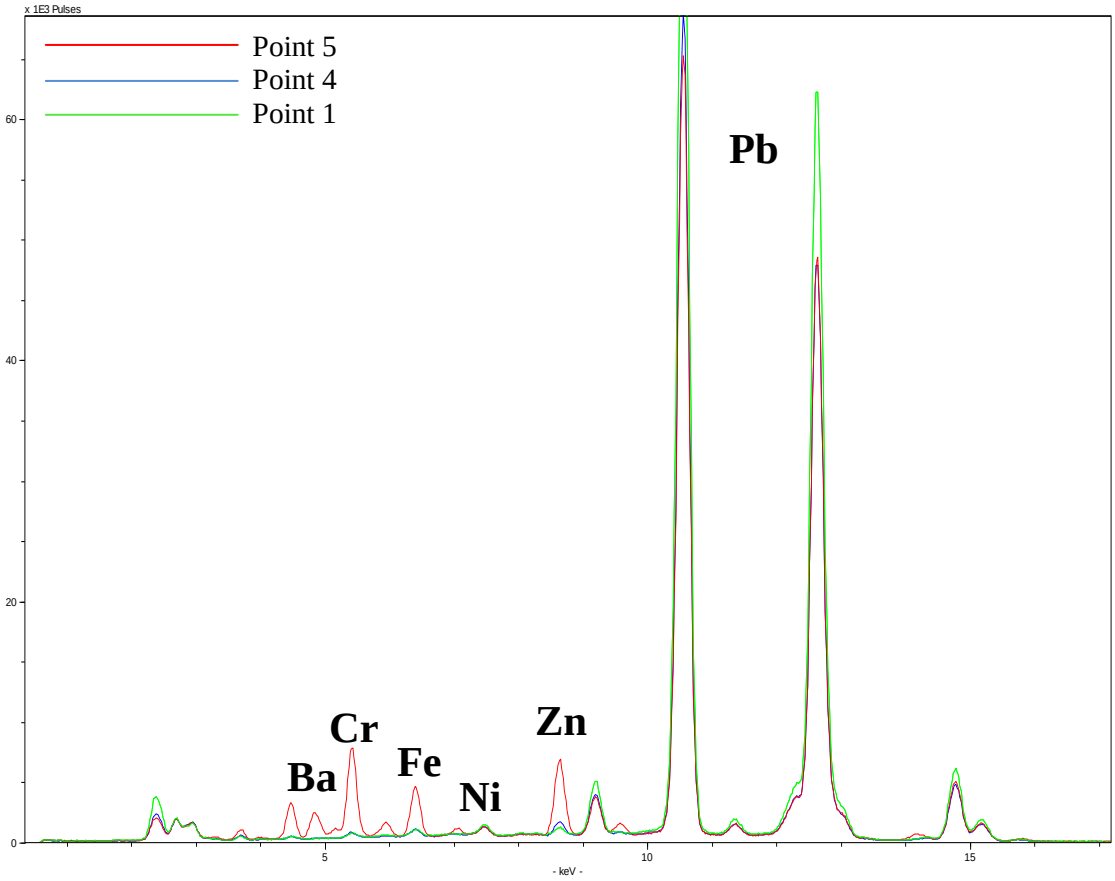

Figure 35. *October, Sullivan Co. NY.* Points 4 and 5, the greens, compared to point 1, white.

Signature

The signature, point 6, compared to the green, point 5, has the highest level of iron of any of the points analyzed (figure 36). This is likely a dark pigment created by blending red ochre with the viridian green.

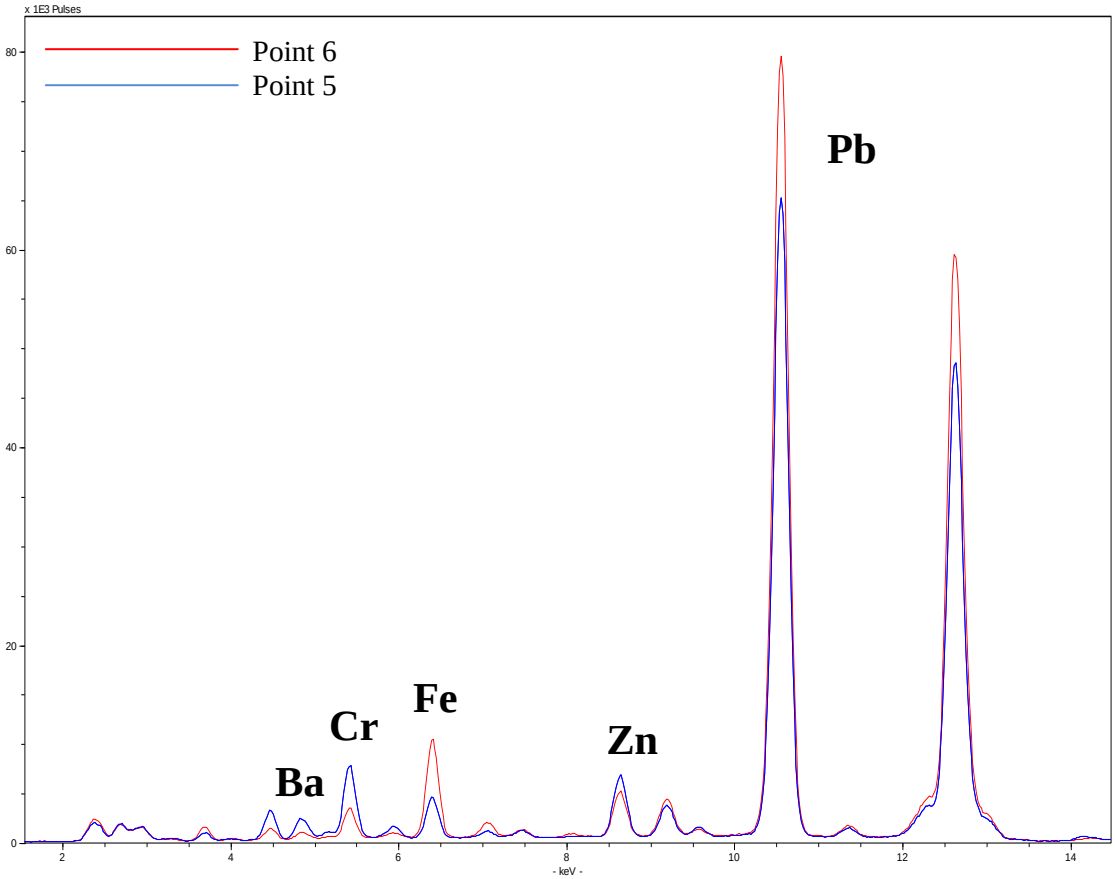

Figure 36. *October, Sullivan Co. NY.* Points 5, the green, compared to point 6, the signature.

June Morning 1909

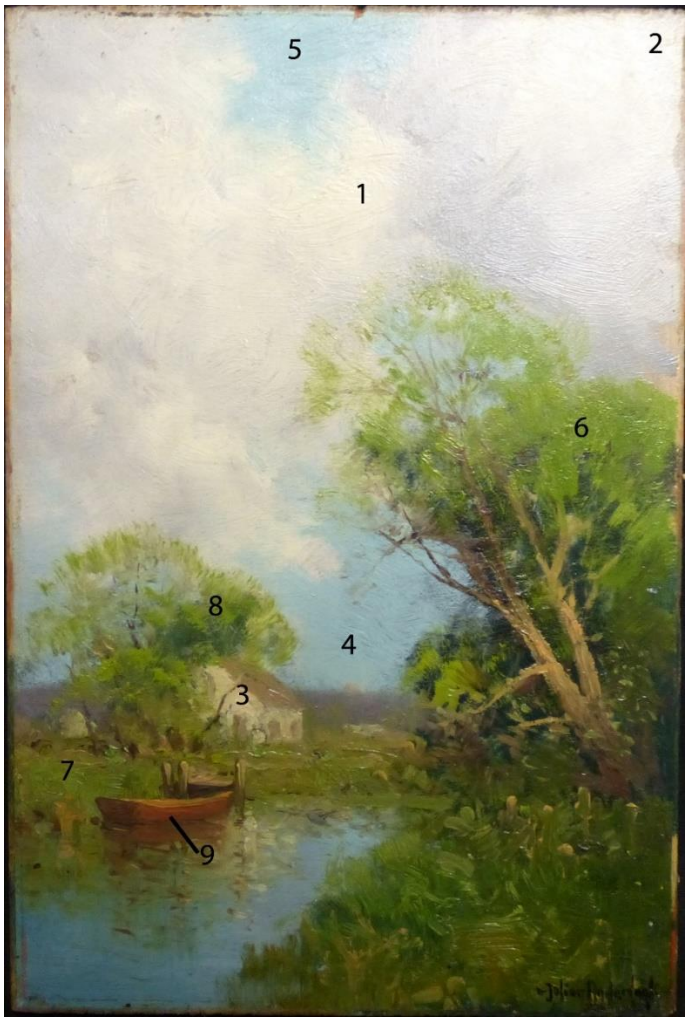

Figure 37. *June Morning, 1909*. 1909, Signed Julian Onderdonk. Oil on wood panel, 9in x 6in, James and Kimel Baker Collection, College Station, TX.

A total of nine points were taken from *June Morning 1909* (figure 37). Points 1 and 2 were of the purest white points in the clouds, point 3 was a very light gray on the house, point 4 and 5 are the blue of the sky, points 6, 7, and 8 were of the greens, and point 9 is the red of the hull of the boat.

White

Points 1 and 2 are very nearly identical, with nothing standing out to set them apart (figure 38). It is a lead-based white with minor energy readings from barium, iron, nickel, zinc, zirconium, cadmium, and tin. The grayish white for point 3 has higher levels of zinc, iron, chromium, and barium than points 1 and 2, likely from the yellows and greens mixed in to achieve the hue needed.

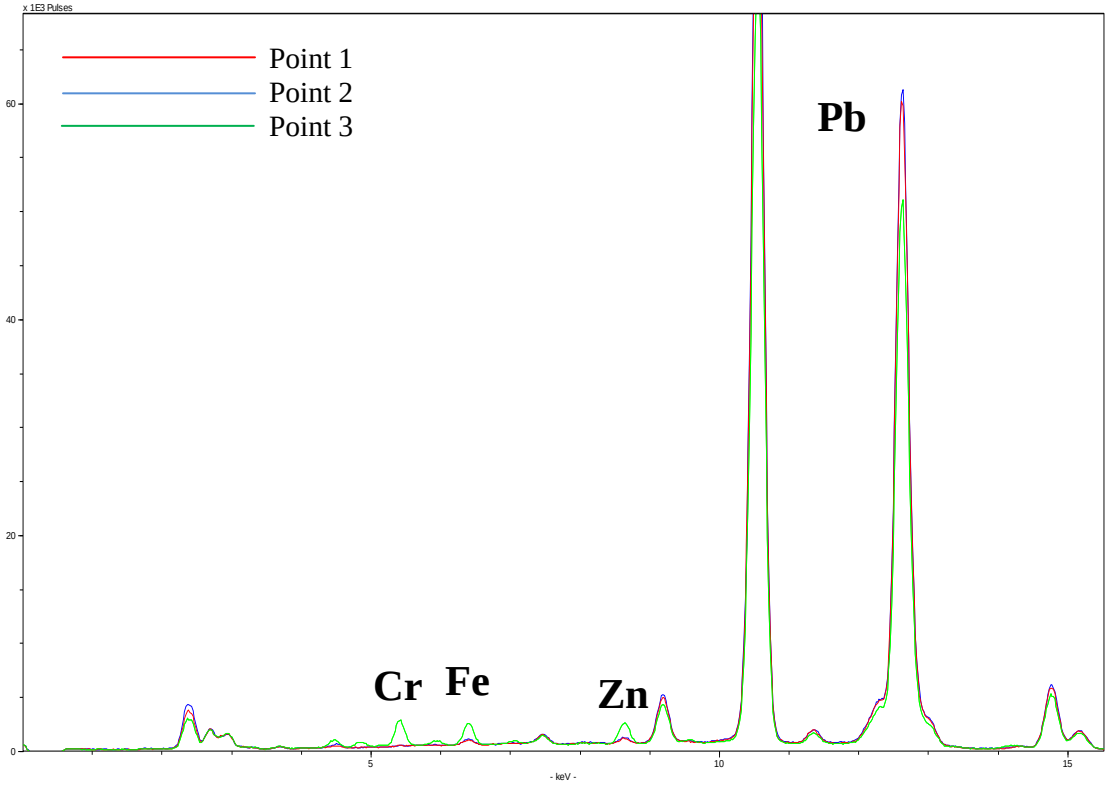

Figure 38. *June Morning, 1909.* Points 1 and 2, white, and point 3, gray.

Blue

Compared to the white points 1 and 2, the blue points of 4 and 5 have higher levels of chromium and zinc (figure 39). The chromium is almost certainly from chromium oxide green. There are traces of calcium, copper, and silicon, which could mean Egyptian blue was used, but the signature is so faint that it seems unlikely for the primary constituent. Instead, the elevated levels of iron likely point to the use of Prussian blue ($Fe_4[Fe(CN)_6]_3$).

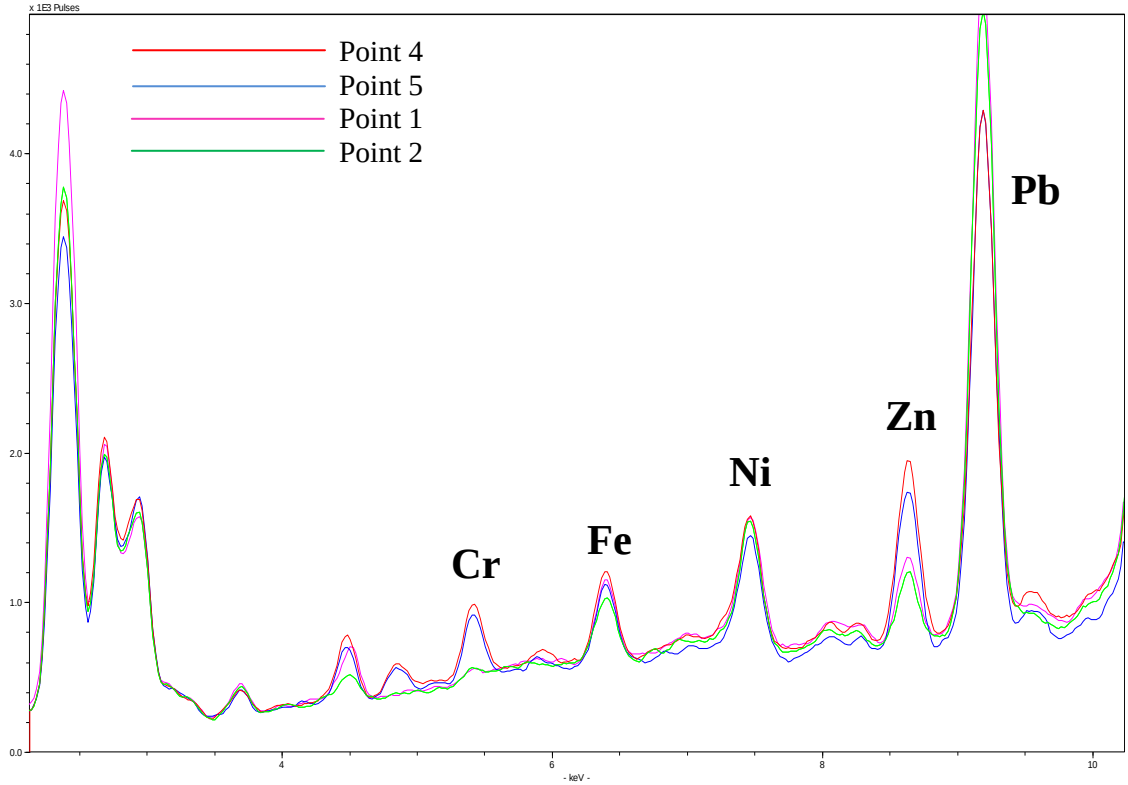

Figure 39. *June Morning, 1909*. Points 1 and 2, white, compared to points 3 and 4, blues.

Green

The spectra for points 6, 7, and 8, the greens, have higher energy signatures for barium, chromium, and zinc than all of the rest of the pigments analyzed (figure 40). The barium is either from Barium white or barium yellow, the zinc could be from zinc white, but the green color itself is almost certainly from the chromium, in the form of chromium oxide green.

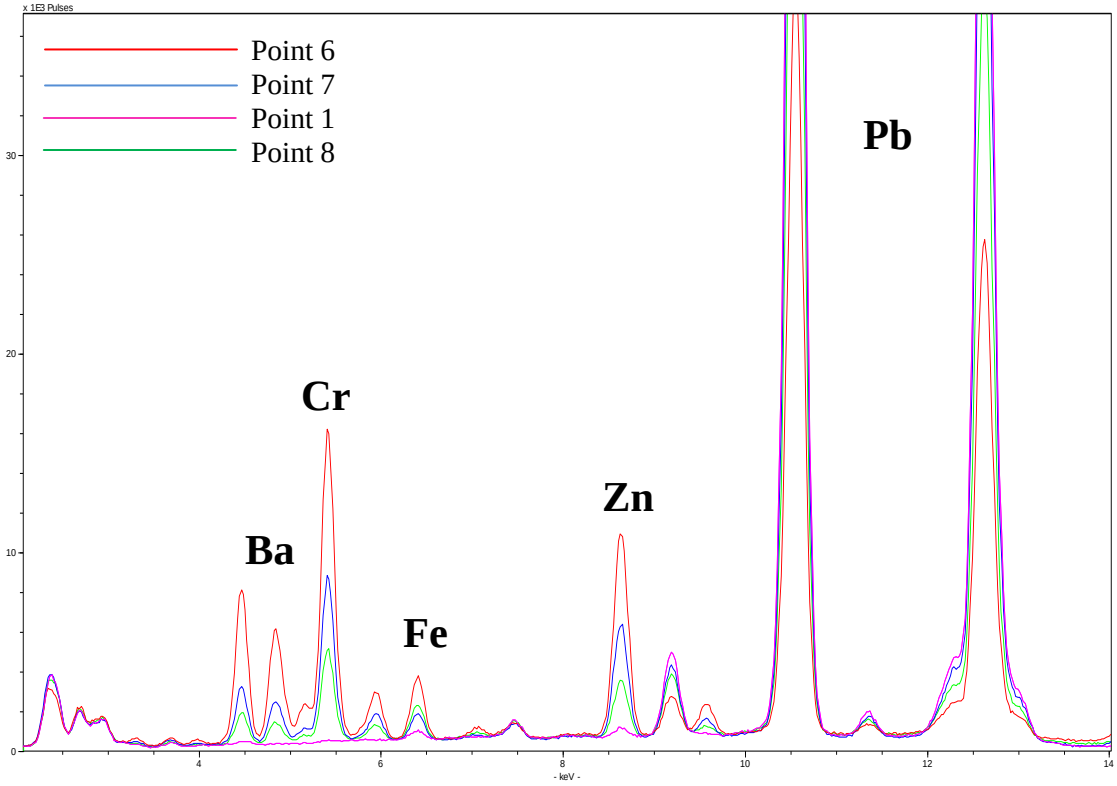

Figure 40. *June Morning, 1909*. Points 6, 7, and 8, greens, compared to point 1, white.

Red

The spectrum for point 9, the red, has the highest peaks for iron and calcium of all the spectra analyzed, which indicates the use of hematite (Fe_2O_3 with clay and quartz). Figure 41 shows the red (in red) compared to the other eight points.

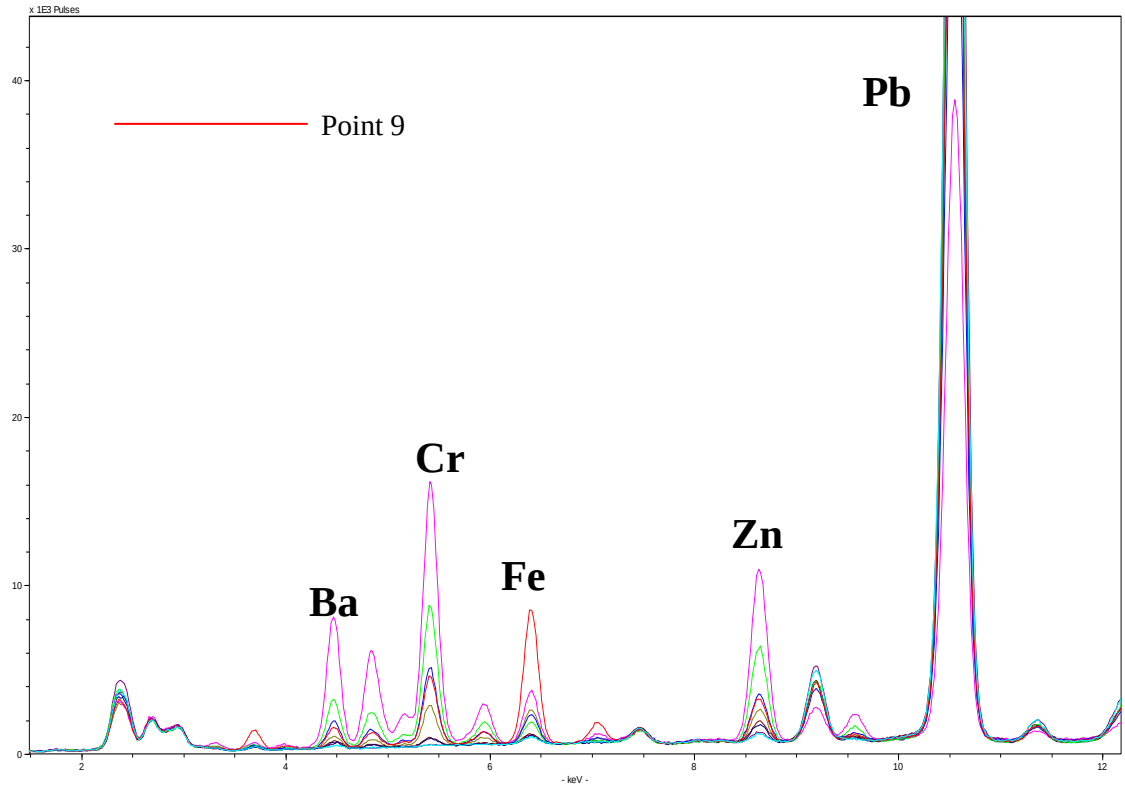

Figure 41. *June Morning, 1909*. Point 9, red, compared to the rest of the points.

Family at Cards

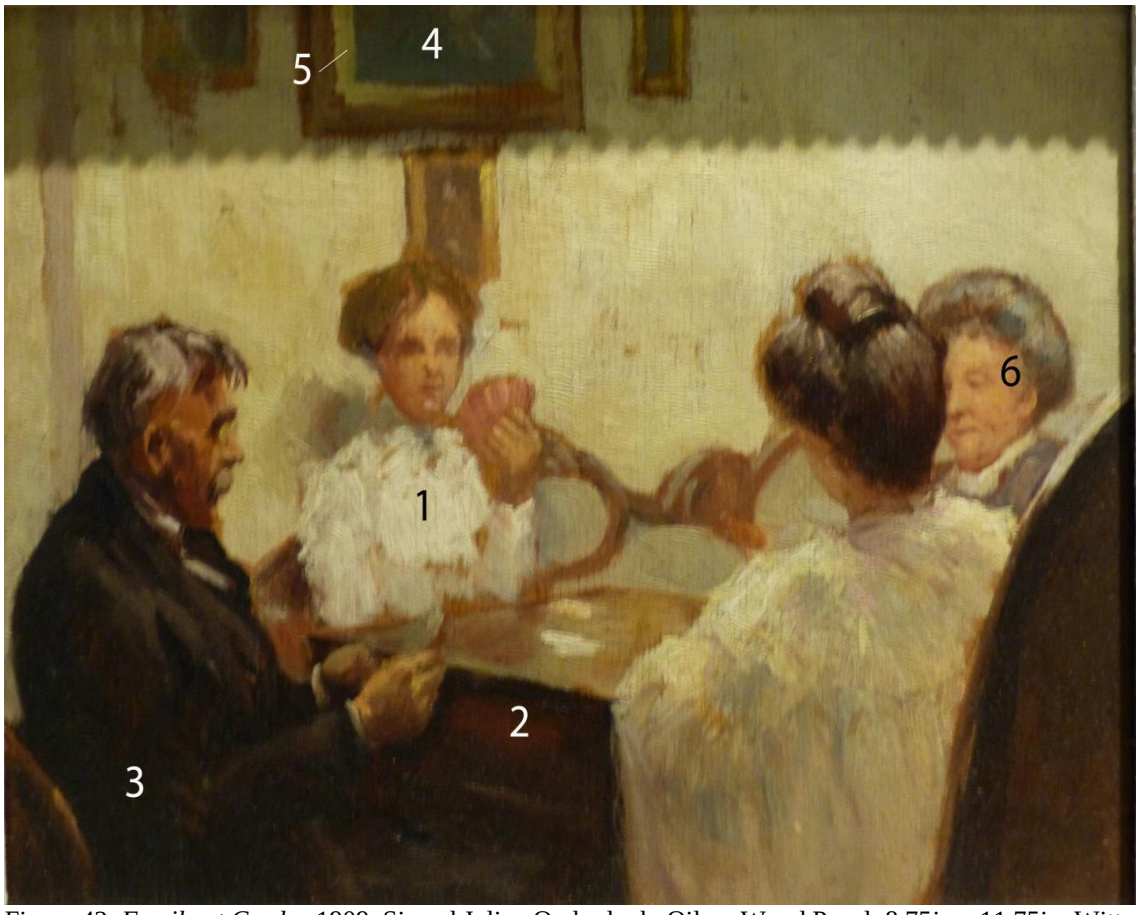

Figure 42. *Family at Cards*. 1909, Signed Julian Onderdonk. Oil on Wood Panel, 8.75in x 11.75in, Witte Museum, San Antonio, TX.

For *Family at Cards* (figure 42), six points were analyzed. (Note: the crenelated shadow at the top of the painting is due to the lighting of the photograph, not the painting itself). Point 1 is the white of the blouse, point 2 is the reddish brown of the table, point 3 is the brown of the coat, point 4 is the blue of the picture in the frame,

point 5 is the yellow of the frame itself, and point 6 is the peach skin tone of the older woman.

White

Point 1, the white of the blouse, is a lead-based white (figure 43). Looking at the blouse, it is evident that a reddish yellow color was painted under it before the white was applied, and this can be seen in the peaks for iron, copper, barium, and zinc.

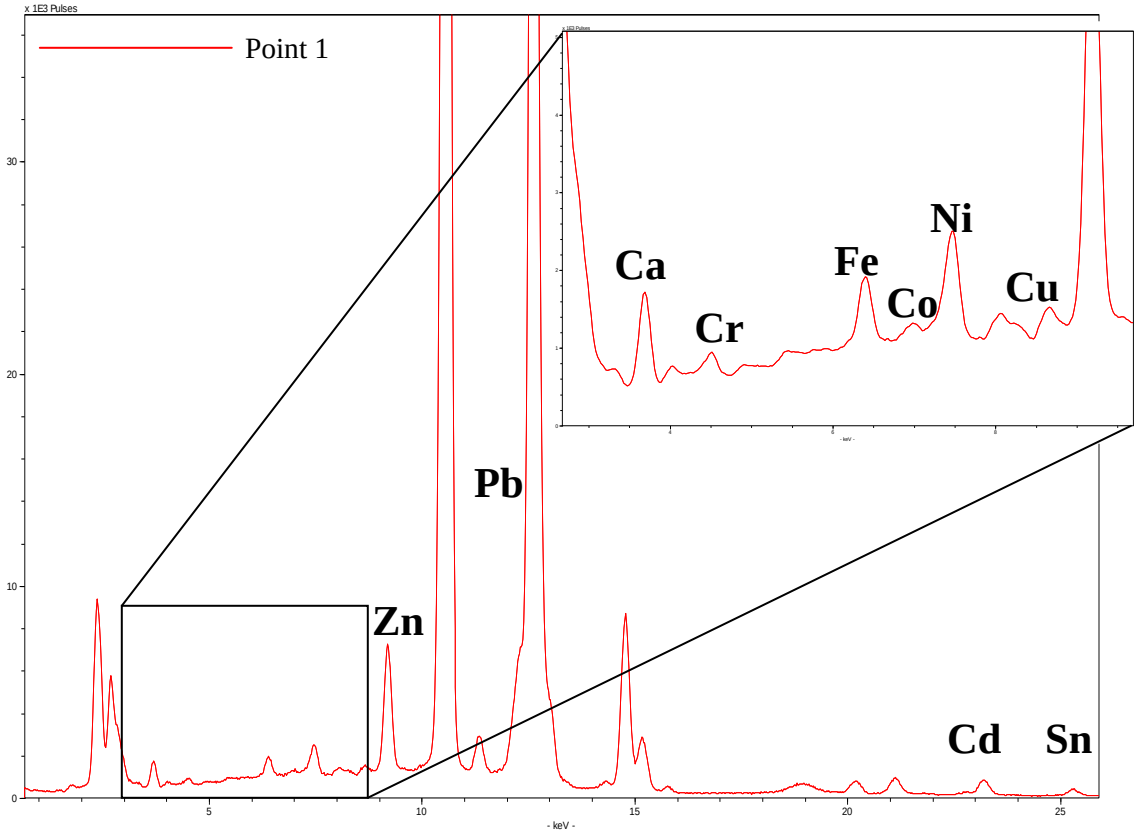

Figure 43. *Family at Cards*. Point 1, white. The inset shows 2-8keV.

Red and Brown

Point 2, the red of the table, and point 3, the brown of the coat, share a base of iron based red, likely a hematite (figure 44). The brown of the coat also has a strong peak for zinc, which indicates the use of a zinc yellow added to the dark red to achieve the orange component of the brown coat. This is consistent with the zinc yellow indications found in the skin tone of point 6.

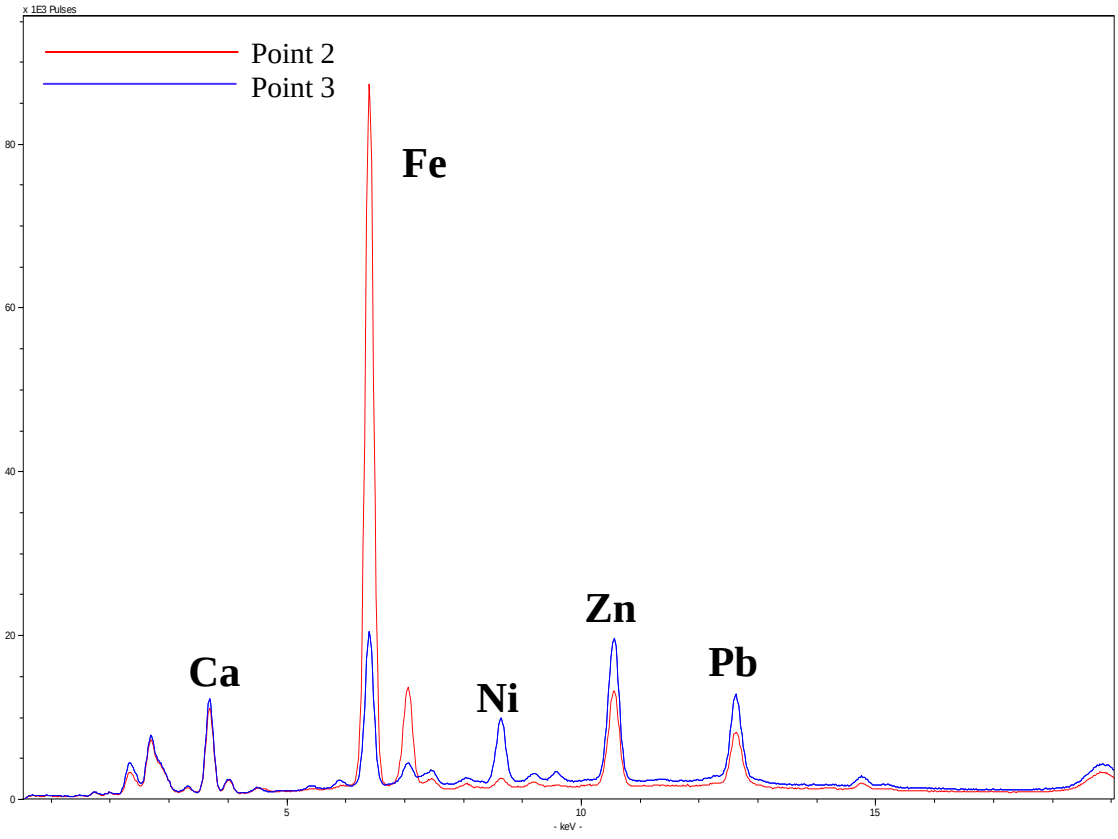

Figure 44. *Family at Cards*. Points 2 and 3, reds and browns.

Gray Blue

Point 4, the bluish gray of the picture in the frame, is a blend of lead white and cobalt blue (figure 45). This is in contrast with the blue used in *June Morning*, also painted in 1909, which was iron-based Prussian blue. Small peaks for iron, zinc, and chromium are also seen, likely hematite red and chromium yellow, similar to the pigments seen in the skin tone of point 6.

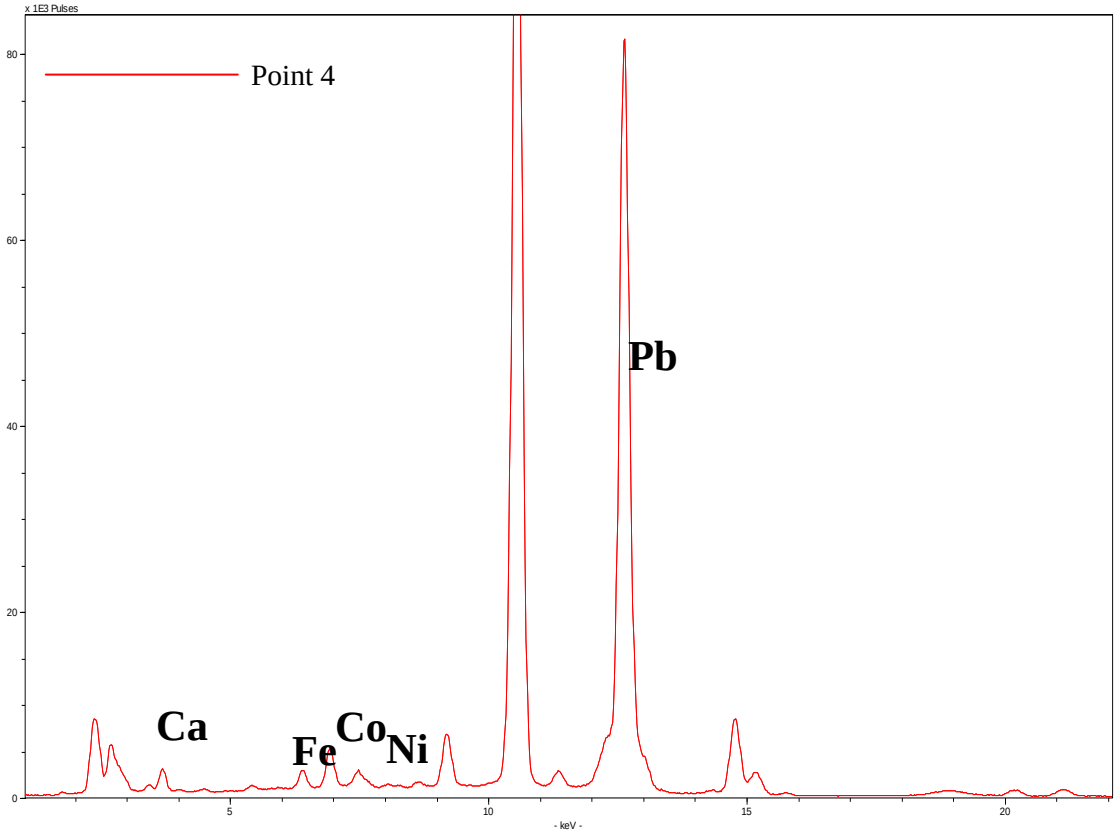

Figure 45. *Family at Cards*. Point 4, blue gray.

Yellow

Point 5, the yellow of the picture frame has a distinct peak for both tin and cadmium. Cadmium yellow (CdS) is a candidate, though the sulfur peak is masked by the Mα-1 peak of lead (figure 46). (The *K*α-1 peak of sulfur is at 2.3084keV, and the *M*α-1 peak of lead is at 2.3423keV) The tin peak, along with the presence of the lead, could indicate the use of lead-tin yellow, though this is unlikely given the history of the pigment. Lead tin yellow was commonly used between the 13th century and the mid-18th century, then was lost and not re-discovered until 1938 by Dr. Richard Jacobi (Wehlte 1975, 91; Douma 2008).

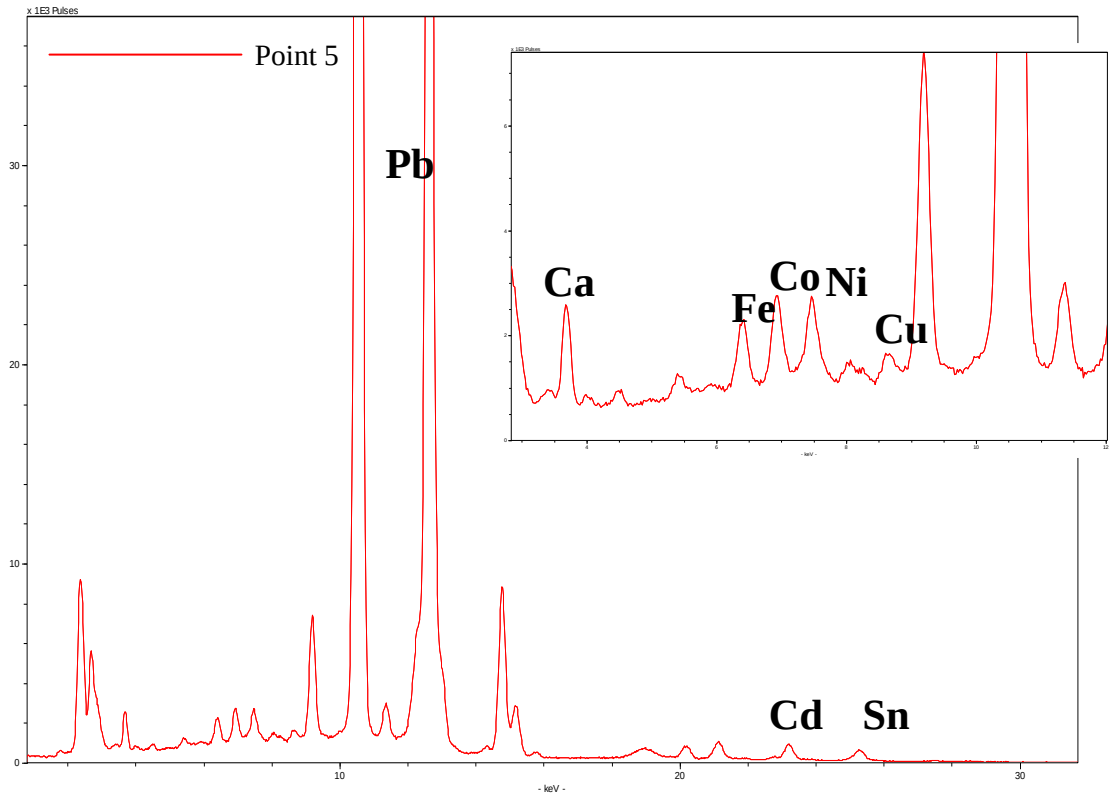

Figure 46. *Family at Cards*. Point 5, yellow. Inset shows 2.5-8keV.

Skin Tone

The skin tone, point 6, is characterized by a strong zinc peak, which dominates the spectra (figure 47). Along with zinc, chromium, iron, nickel, and lead are present. As seen above, the red is iron-based. The zinc and chromium are indicative of zinc yellow (ZnCrO4), though this would signify that a different yellow was mixed to make the skin tone than the yellow used for the picture frame. The lead is likely lead white again ($Pb_3(CO_3)_2(OH)_2$). Nickel, seen in each of the spectra for this painting, is only used in the formulation of modern pigments in the manufacture of nickel yellow, ($Ni_3(PO_4)_2$), known since 1901, and azo-pigment group metal complex sub-group of pigments. Though the nickel based pigments in the metal complex sub-group of the azo-pigment group were discovered in 1885, they were not produced commercially until 1921, 12 years after this painting was completed (Eastaugh et al. 2008, 37, 282.) The nickel yellow is possible, given the time frame, but given the consistency of the nickel peak throughout the painting, it is more likely a constituent of the board that was painted on than the painting itself.

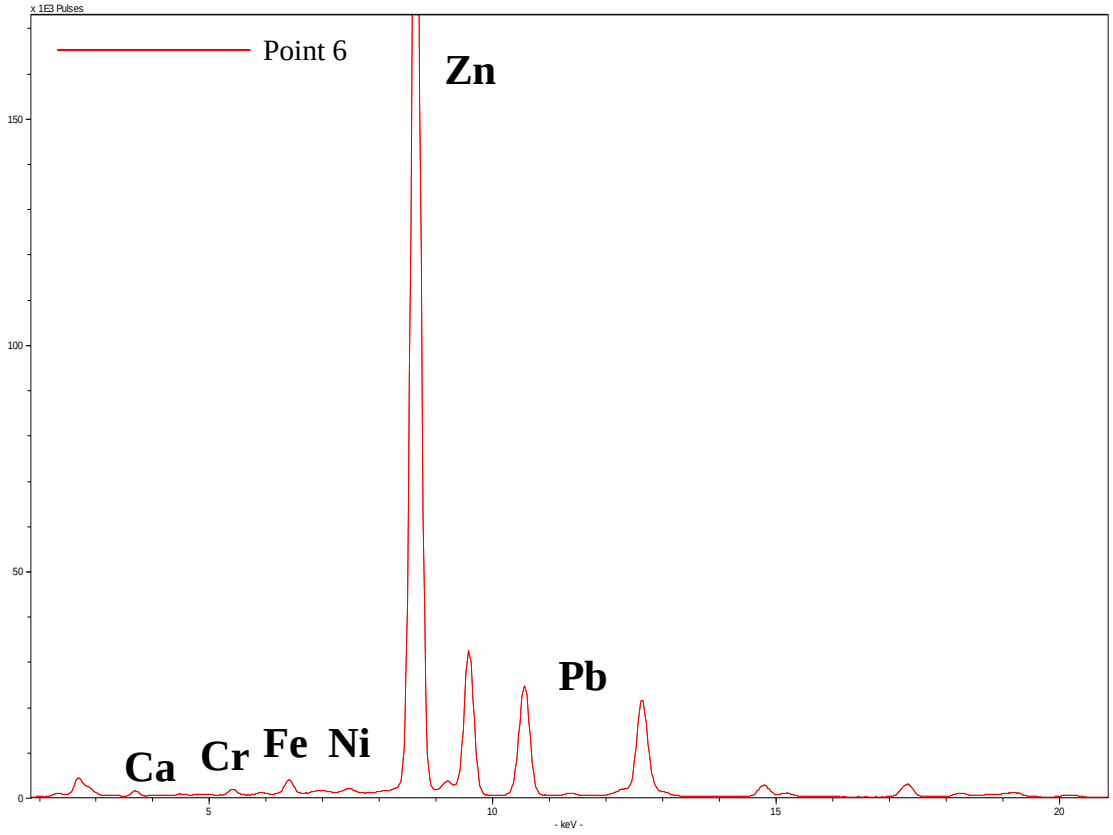

Figure 47. *Family at Cards*. Point 6, skin tone.

Bluebonnets and Cacti

Figure 48. *Bluebonnets and Cacti*. 1910, signed Julian Onderdonk, Oil on Canvas, 16in x 24in, Villa Finale, San Antonio, TX.

A total of seven points were taken for *Bluebonnets and Cacti* (figure 48). Points 1 and 5 are the blues of the flowers, point 2 is the red of the tree trunk, point 3 is the reddish yellow of the road, point 4 is the green of the foliage, and point 6 is the signature. Each point analyzed has a peak for zinc and lead, indicating a zinc and lead white primer was used on this painting.

Blue

Points 1 and 5 are blues of the bluebonnets. The blue pigment is difficult to isolate, because the elements seen in the scans that can comprise blue pigments do not vary between the different points. Iron, which is used for Prussian blue, is consistent across all points. Moreover, it is almost certainly the source of the red pigment, which is prevalent across the painting. Despite the fact that the peaks appear with the same intensity across all points, the most likely candidate for the blue is cobalt blue. Points 1 and 5 also have similar peaks for strontium, seen below; this is strontium yellow pigment (figure 49).

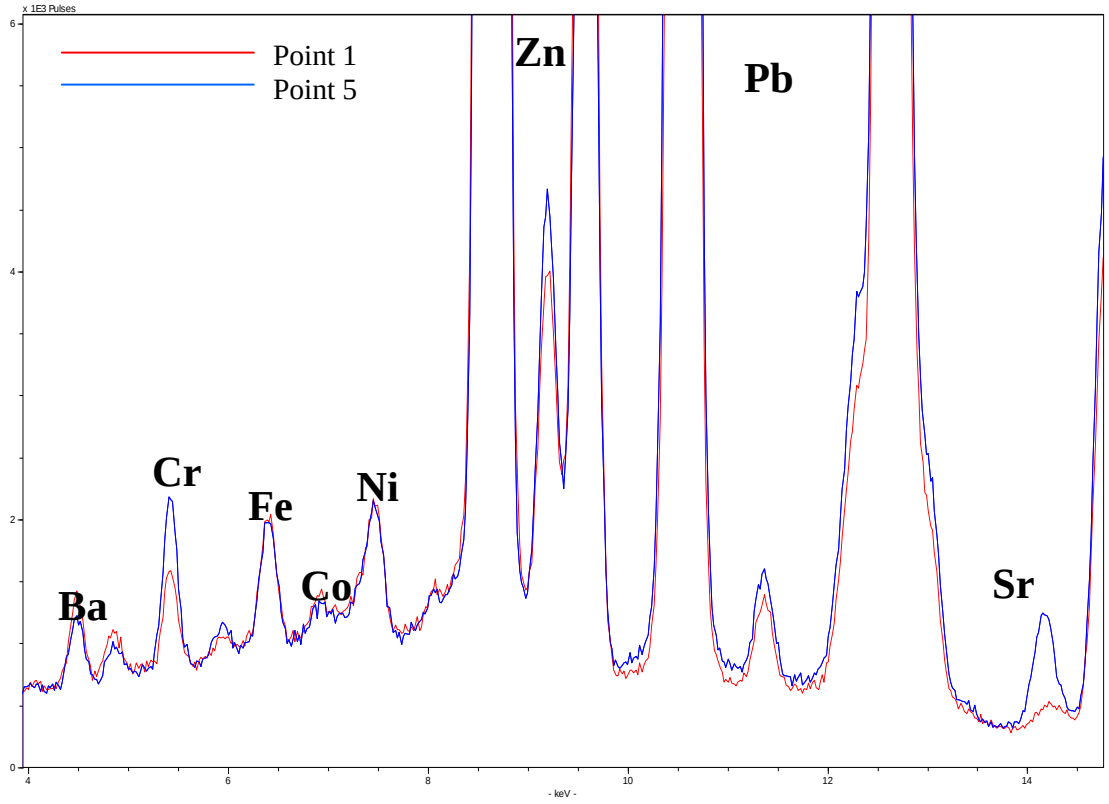

Figure 49. *Bluebonnets and Cacti*. Points 1 and 5, blues.

Red, Green, and Yellow

Point 2, the red of the tree is likely an iron-based red (figure 50). That said, it is not distinct enough to be certain. The point is not especially vibrant, and it is obviously mixed well with other colors, making definitive identification impossible. Point 4, the green of the foliage, is most likely viridian, a chromium-based green (Cr2O3). Point 3, the yellow of the path, has a very similar spectrum to point 4, though point 4 has higher peaks for iron, chromium, strontium. Strontium is a good candidate, as is cadmium. Both elements can only be found either in white or yellow pigments, as well as other pigments using the white or yellow to lighten them (Eastaugh 2008, 75, 361).

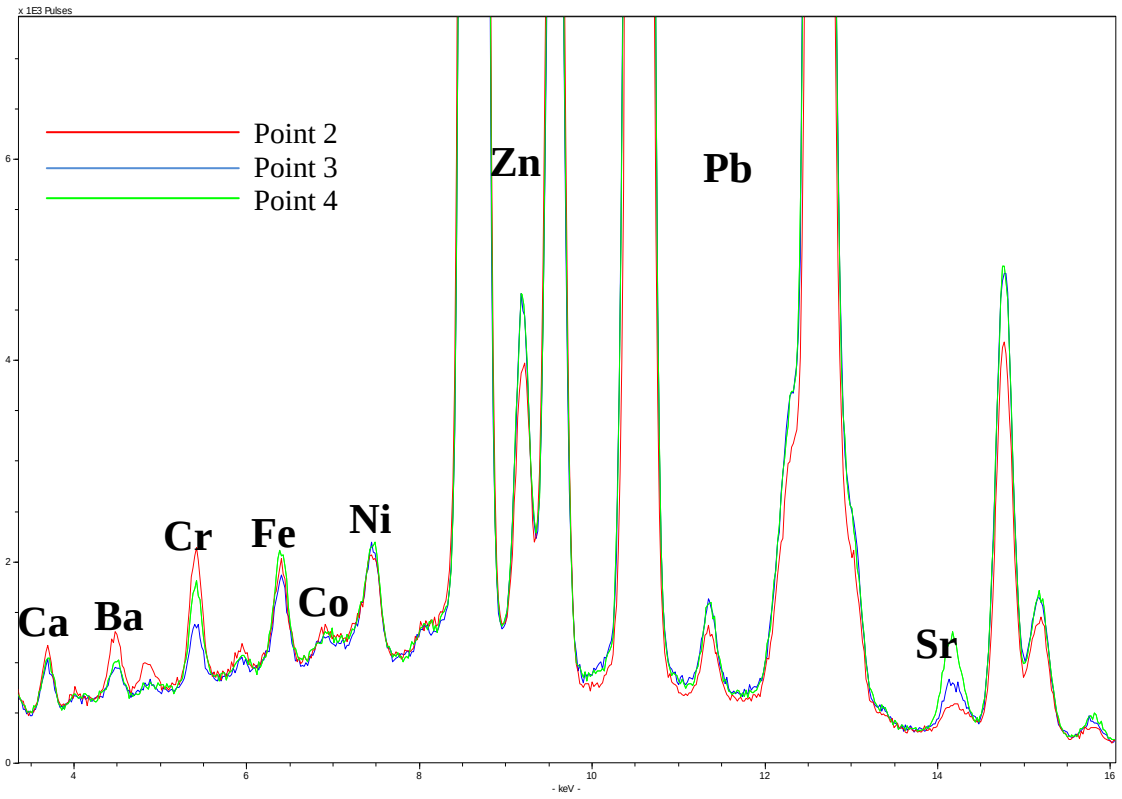

Figure 50. *Bluebonnets and Cacti*. Points 2, 3, and 4, red, green, and yellow, respectively.

Signature

The spectrum for the signature is very similar to points 1 and 5, though both 1 and 5 have higher peaks for chromium (figure 51). The dark for the signature is either a blend of the above mentioned paints to make a dark color, or an organic based black that is not readable by the XRF.

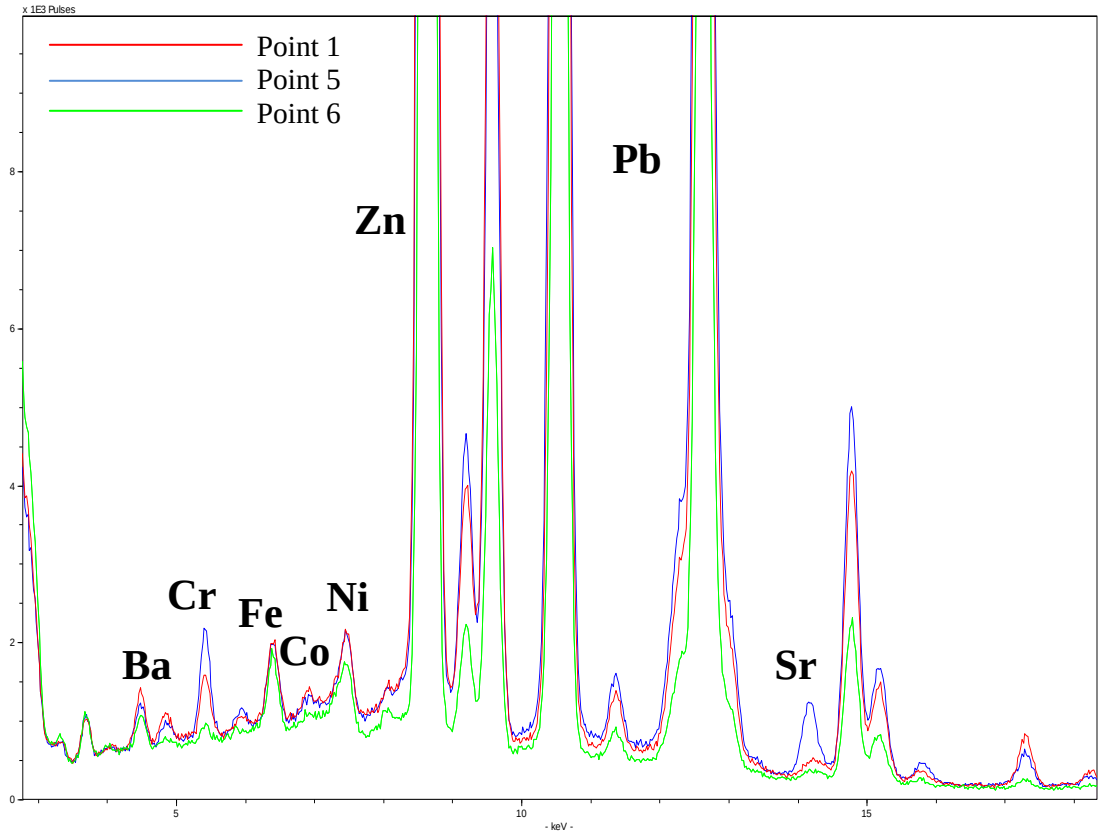

Figure 51. *Bluebonnets and Cacti*. Points 1 and 5, the blues, compared to point 6, the signature.

Bluebonnet Field

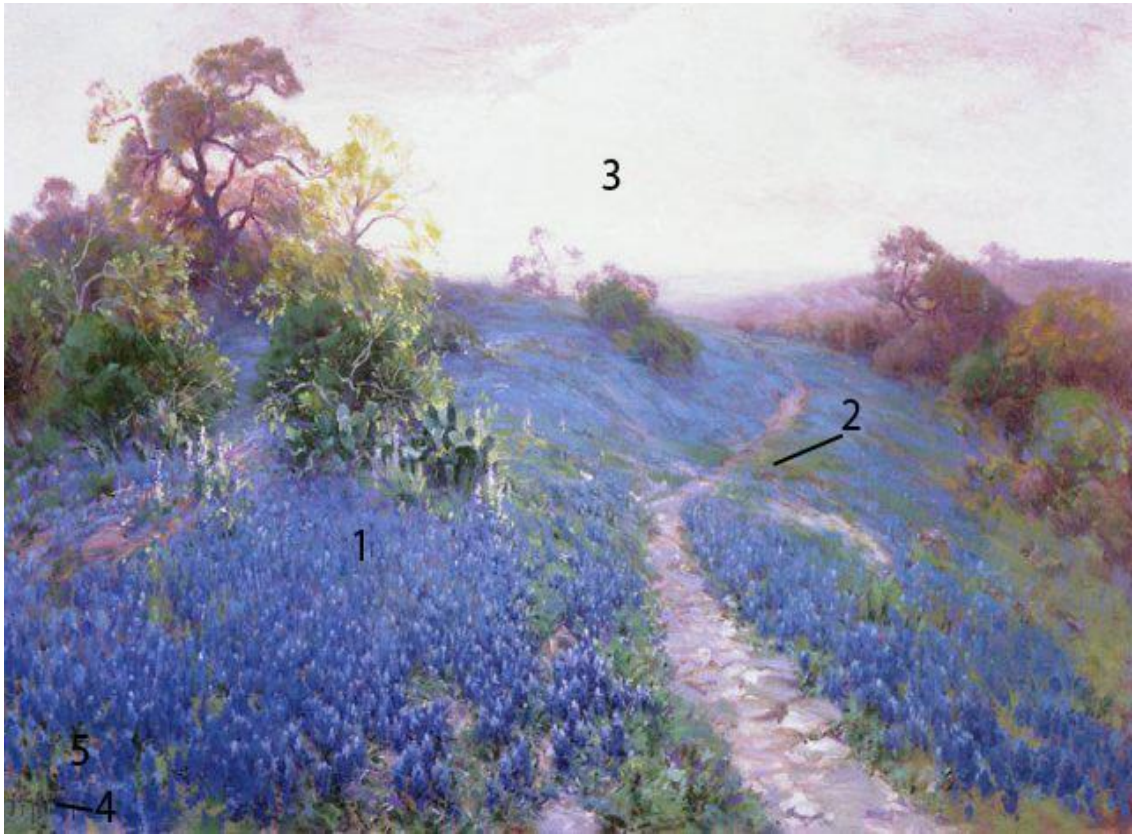

Figure 52. *Bluebonnet Field*. 1912, signed Julian Onderdonk, Oil on Canvas, 20in x 30in, Witte Museum, San Antonio, TX.

A total of five points were analyzed for *Bluebonnet Field* (figure 52). Point 1 and 4 are the blues of the flowers, point 2 is the green of the grass in the path, point 3 is the yellow and white of the sky, and point 5 is the signature. This painting was primed with a lead-based white primer based on the lead peak in each point.

Blue and Green

Points 1 and 4 are the blues of the bluebonnets, and point 2 is the green grass on the path. Point 4 also has green around it, and this is reflected in its analysis. The blue pigment is primarily a cobalt based blue, and given the presence of tin, it is likely cerulean blue (CoO $nSnO_2$), which was first marketed in London in 1859 (Eastaugh 2008, 96). Looking at point 2, and also the green that is behind the blue in point 4, there are peaks for chromium, strontium, and zinc (figure 53). This indicates that the green is either a chromium based green like viridian (Cr_2O_3) with a zinc white to lighten it, or a mixture of cobalt blue mixed with zinc yellow ($ZnCrO_4$) and strontium yellow ($SrCrO_4$).

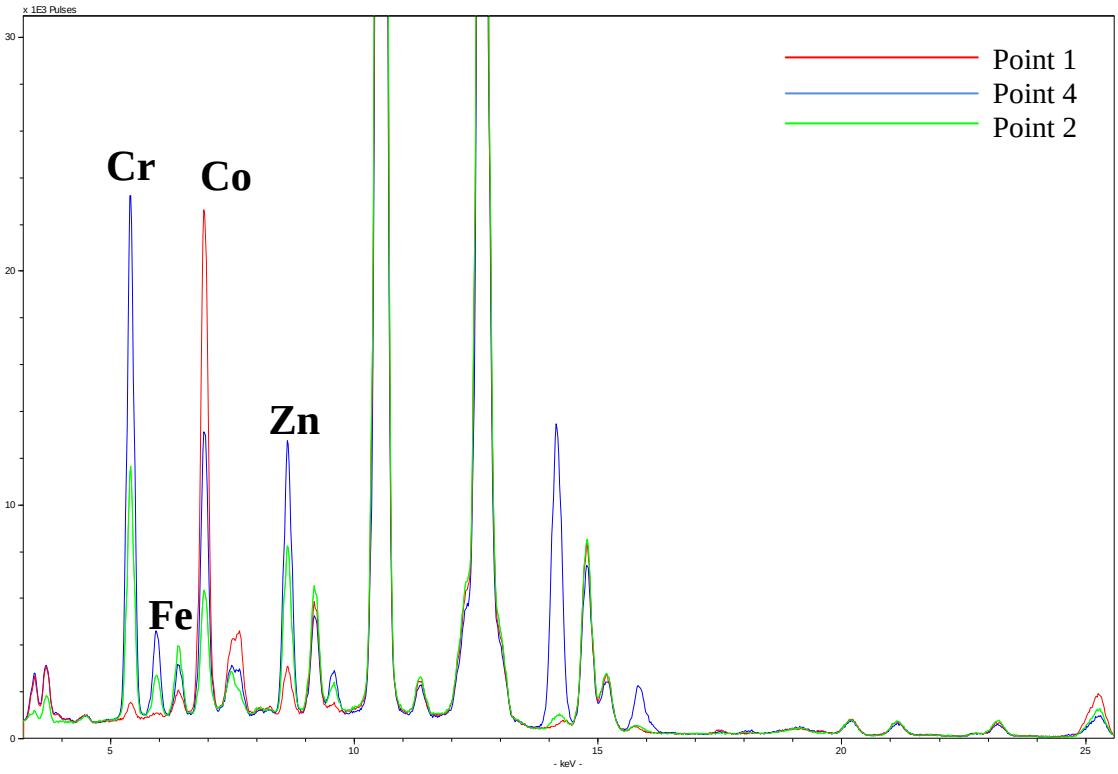

Figure 53. *Bluebonnet Field*. Points 1 and 4, the blues, and point 2, the green of the path.

Yellow and White

The greens in points 2 and 4 showed evidence for zinc and strontium based yellows mixed with cobalt blue (figure 54). The yellowish white of the sky of point 3 does not show chromium, but instead has the highest peak for cadmium. Cadmium yellow (CdS) is certainly a possibility, though if mixed with lead, cadmium yellow leads to chalky discoloration due to the creation of lead sulfides (Eastaugh et al. 2008:72). Given the subtleness of the yellow in the white of the sky though, this is the most likely candidate for point 3. The white, as mentioned in the introductory paragraph for this painting, is lead white.

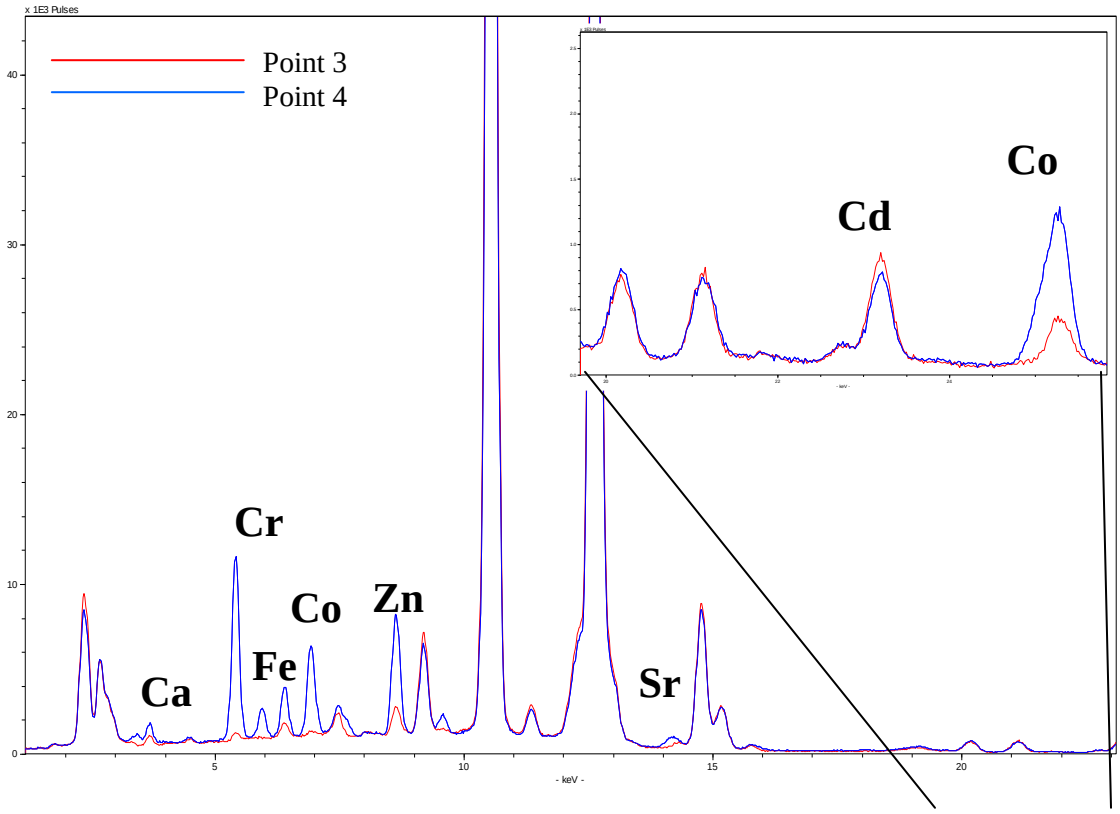

Figure 54. *Bluebonnet Field*. Point 3, yellow white of the sky compared to point 4, blue.

Signature

The signature is directly atop the blue and green background of point 4, so it comes as little surprise that the 2 spectra are very similar (figure 55). Point 5, the signature, has more red iron based pigment, as well as more cobalt. This indicates that the dark brown of the signature is likely a mix of hematite (Fe_2O_3) and cerulean blue (CoO SnO_2).

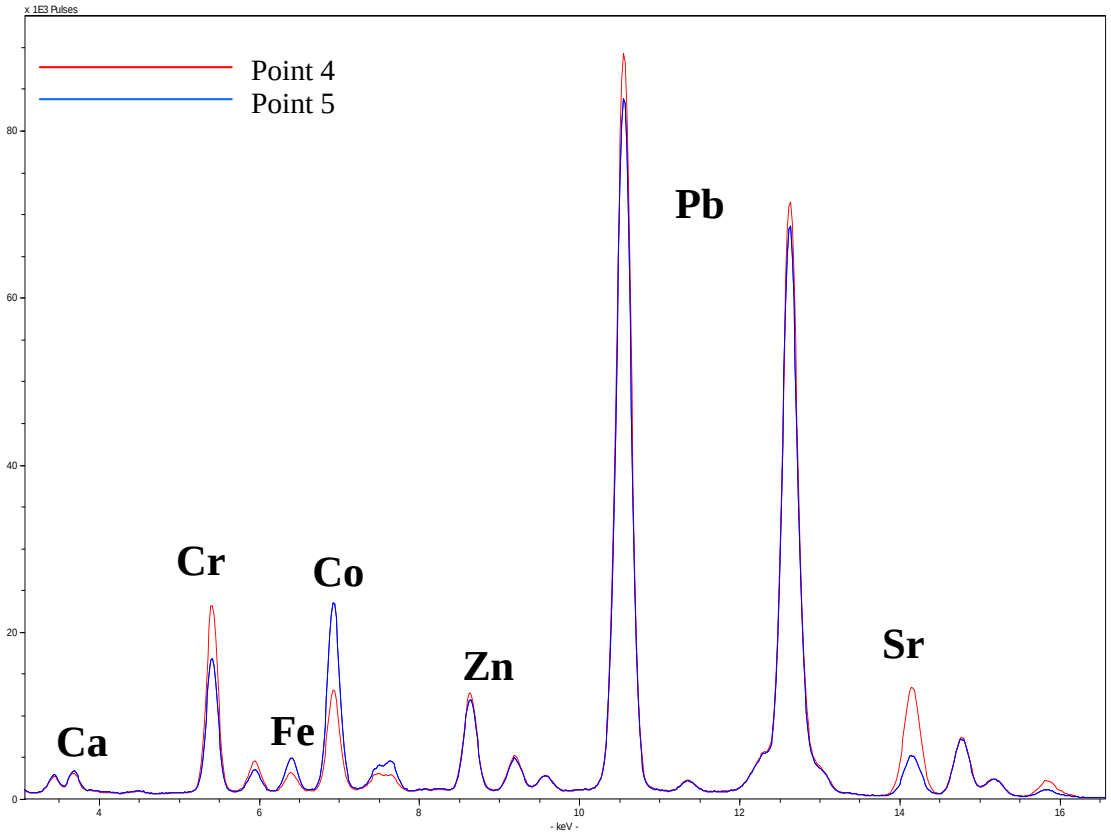

Figure 55. *Bluebonnet Field*. Point 5, the signature compared to point 4, blue.

A Pool on the Guadeloupe

Figure 56. *A Pool on the Guadeloupe*. 1913, Signed Julian Onderdonk, Oil on Canvas, 25in x 30in, Villa Finale, San Antonio, TX.

A total of five points were analyzed for *A Pool on the Guadeloupe* (figure 56). Point 1 is the lightest white/blue part of the water, point 2 is the yellowish white of the sky, point 3 is the orange and red of the leaves on the bottom right, point 4 is the dark red of the leaves in the top right, and point 5 is the dark blue of the bottom left of the painting. Though each spectrum contains peaks for both zinc and lead, the primer for this painting is likely lead white. The zinc peak varies with each point, whereas the lead is consistent, only elevated in the yellowish white of point 2.

White and Blue

Point 1 is a mixture of white and blue, and point 5 is the dark blue of the water. Both areas are complex; there are greens, yellows, and reds visible, but by comparing points 1 and 5 with the other points, the white and blue pigment sources are separable from the others. Point 1 is dominated by the peak for zinc (Zn), which indicates that although a lead white primer was used, zinc white was utilized in the painting as well. Point 5 has high peaks for tin, chromium, iron, and cobalt (figure 57). The cobalt and the tin are indicative of cerulean blue, (CoO SnO2), the chromium is likely chromium oxide green (Cr2O3), and the iron is hematite.

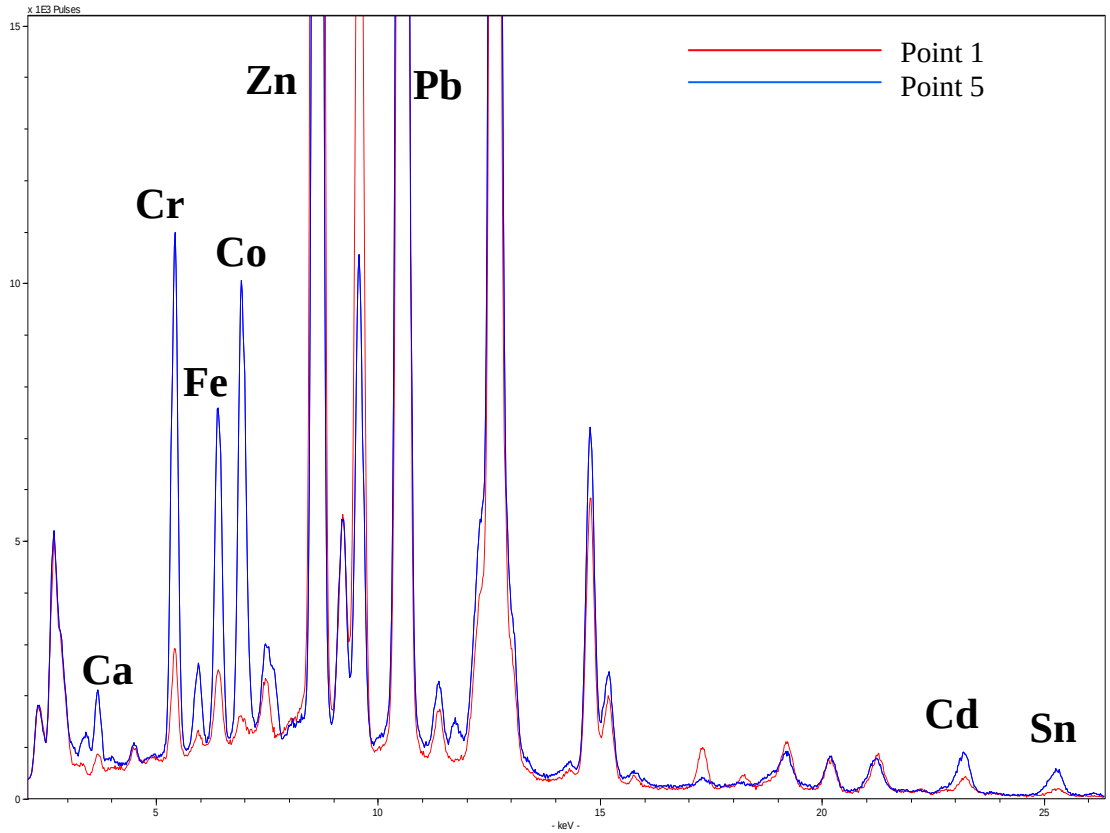

Figure 57. *A Pool on the Guadeloupe*. Point 1, white, compared to point 5, blue.

Yellow and Red

The reds of points 3 and 4 are iron based hematite. The orange tint is likely from a blend of the red and yellow, and compared to points 3 and 4, point 2, the pale yellow of the sky, is higher in zinc (figure 58). This indicates the use of zinc yellow (ZnCrO), which may have been in the 1912 painting *Bluebonnet Field*, but prior to that was only seen in the skin tone of the 1909 piece *Family at Cards*. The signature for zinc is very strong for both the reddish orange and the dark red, though the peak is higher for the reddish orange, indicating more zinc yellow.

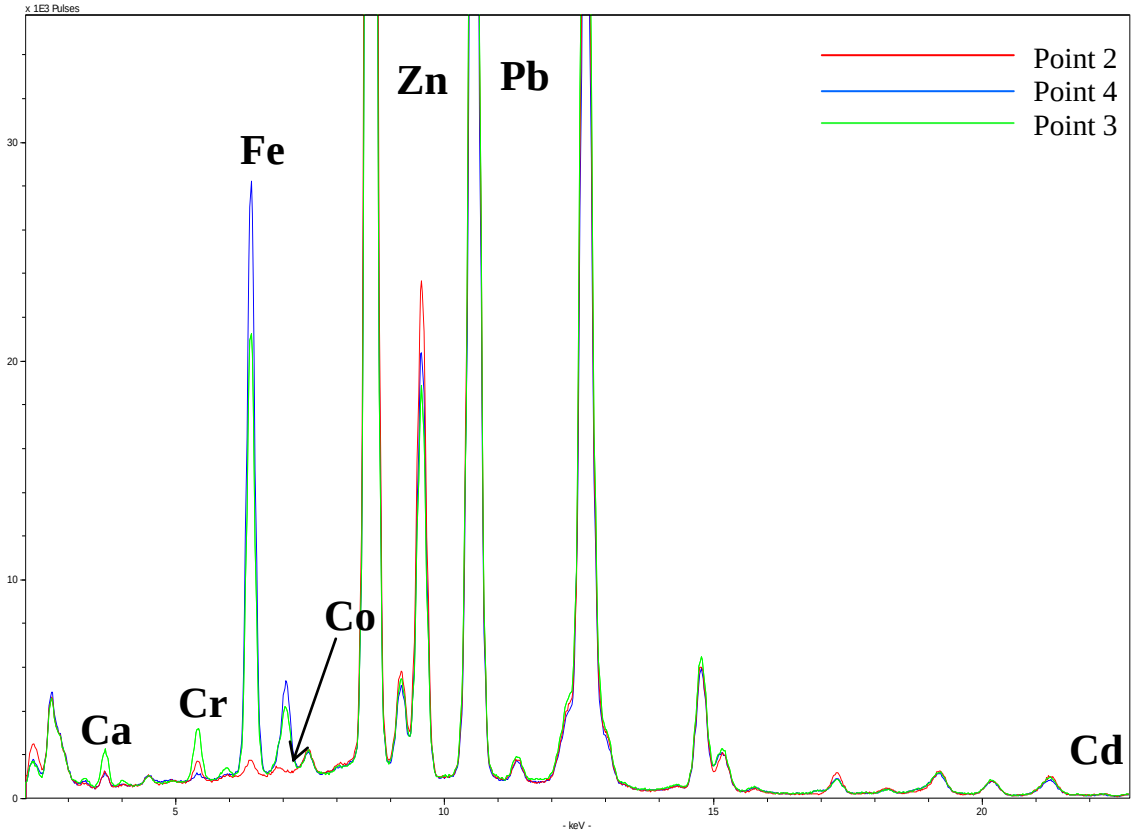

Figure 58. *A Pool on the Guadeloupe*. Points 3 and 4, red and orange, and by proxy, yellow.

Afternoon Back of Laurel Heights

Figure 59. *Afternoon Back of Laurel Heights*. 1913, Signed Julian Onderdonk, Oil on Wood Panel, 8in x 11in, Witte Museum, San Antonio, TX.

For *Afternoon Back of Laurel Heights* (figure 59), eight points were analyzed. Point 1 is the white is of the sky, points 2 , 3, and 7 are various hues of green, point 4 is the signature, point 5 is the orange of the bush, point 6 is the dark violet color in the shadow of the tree, and point 8 is the violet of the bush.

White

The white in point 1 is either zinc white, lead white, or both (figure 60). The lead peaks are more consistent across the painting than the zinc peaks, so the more likely scenario is a lead white primer and a zinc white paint.

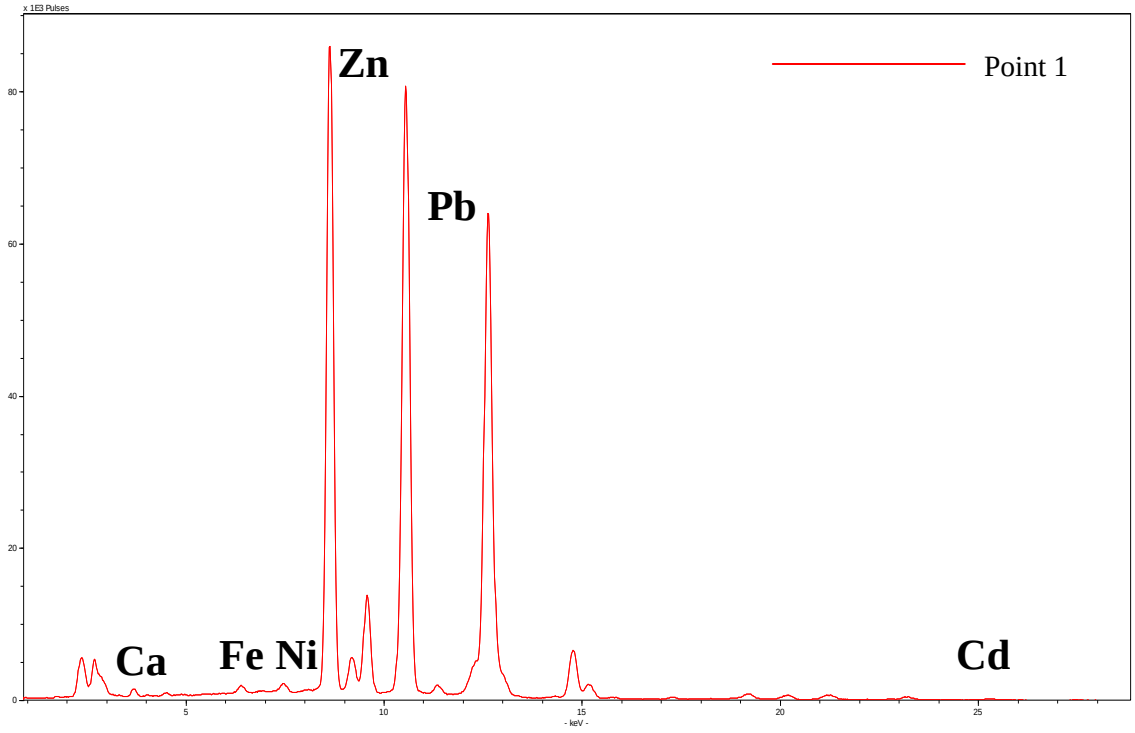

Figure 60. *Afternoon Back of Laurel Heights*. Point 1, white.

Green

Points 2, 3, and 7 are the various hues of green found in the painting. Across the three points, the consistent peaks are for iron and chromium (figure 61). This could indicate one of two things, chromium oxide green is being used, or zinc yellow ($ZnCrO_4$) is being mixed with Prussian blue ($Fe_4[Fe(CN_6)]_3$ and $14\text{-}16H_2O$). Prussian blue is seen in many of Onderdonk's work, though the presence of cobalt in points 3 and 4 suggest that cobalt blue was being used, not Prussian. Another possibility for the cobalt in point 3 is cobalt yellow ($K_3[Co(NO_2)_6]$ $1.5H_2O$), though the presence of cadmium in the lighter green suggests that cadmium yellow is being used, not cobalt yellow. Chromium oxide green is the most likely candidate, mixed with cobalt blue for the darker colors, and cadmium yellow and zinc yellow are used to lighten the hue in point 2.

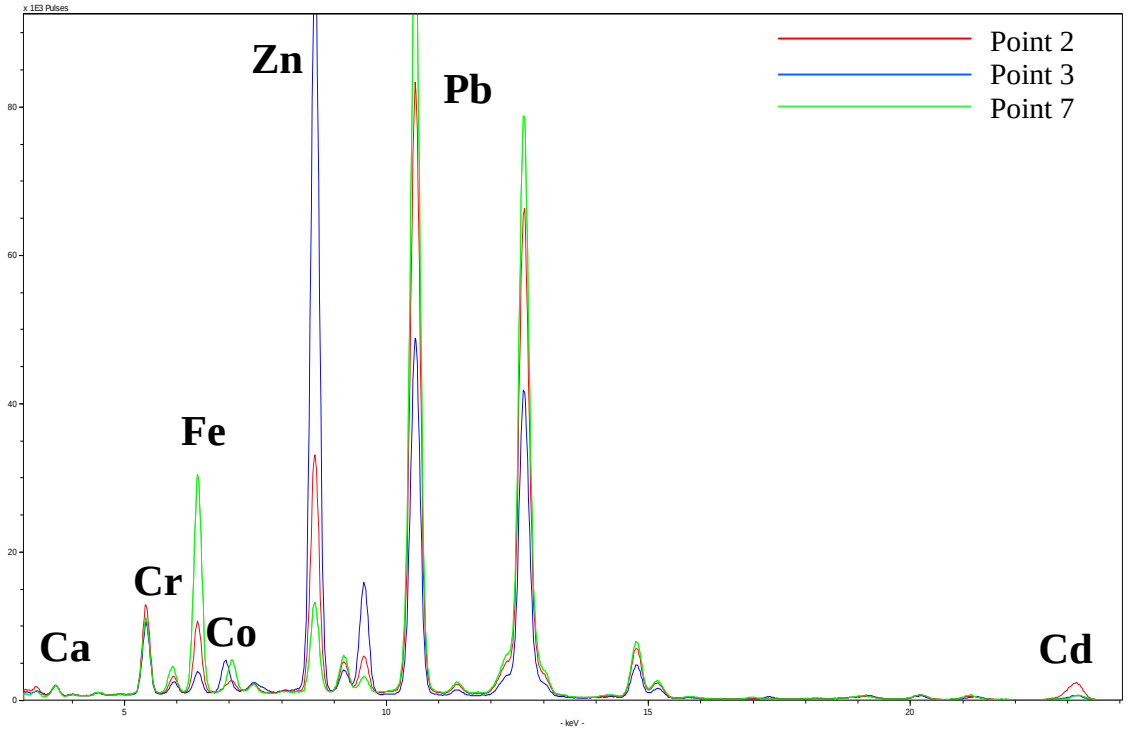

Figure 61. *Afternoon Back of Laurel Heights*. Points 2, 3, and 7, hues of green.

Orange and Violet

The orange of point 5 is a mixture of iron based red and zinc yellow (figure 62). Point 5 also had a strong peak for manganese and phosphor where it was painted over some of the violet seen in point 6; this is indicative of manganese violet, (chemical composition is debatable, but it is a manganese phosphate, possibly a double salt manganese ammonium pyrophosphate), which was introduced by Leykauf in 1868 (Wehlte 1975, 156) . This is the earliest painting of Onderdonk's dated work that contains the signature peaks for manganese violet. Point 6 and 8 also have the peaks for manganese violet, as well as zinc, cadmium, chromium, cobalt, and iron. This indicates the use of the above mentioned reds, yellows, greens, and blues to achieve the darker shades of violet.

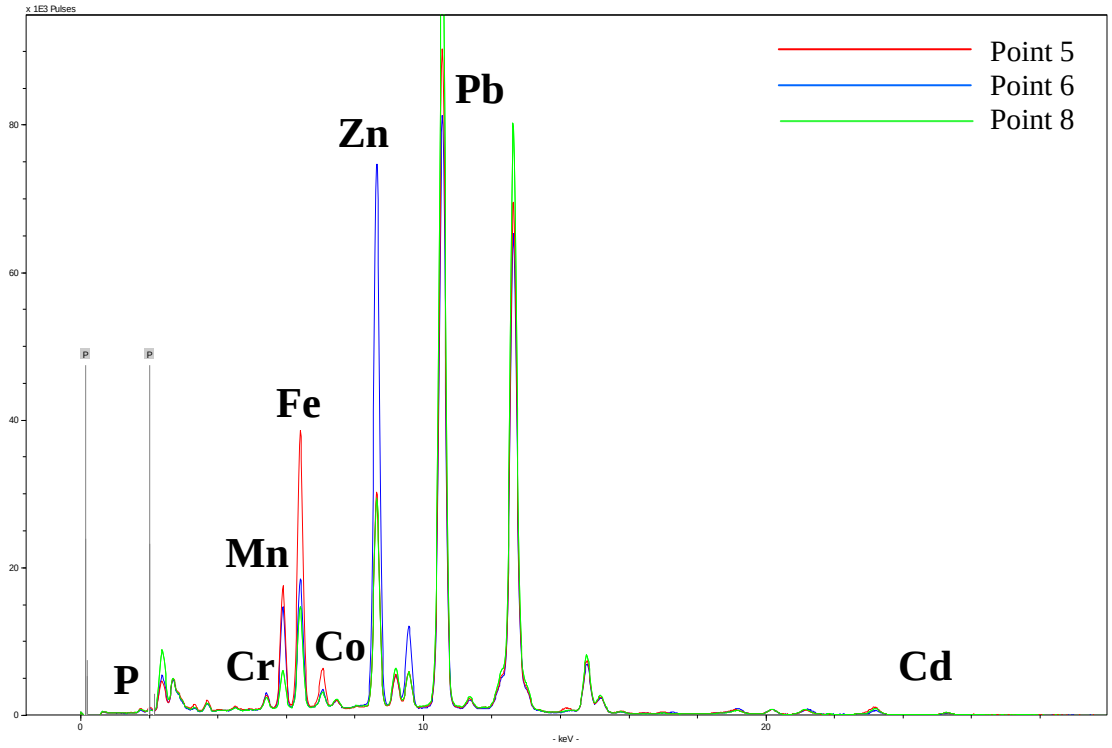

Figure 62. *Afternoon Back of Laurel Heights*. Point 5, orange, and points 6 and 8, violet.

Signature

There are two main elemental differences between the spectra of points 3 and 4. Point 4 has higher peaks for iron and cobalt, and point 3 has a higher peak for zinc and chromium (figure 63).

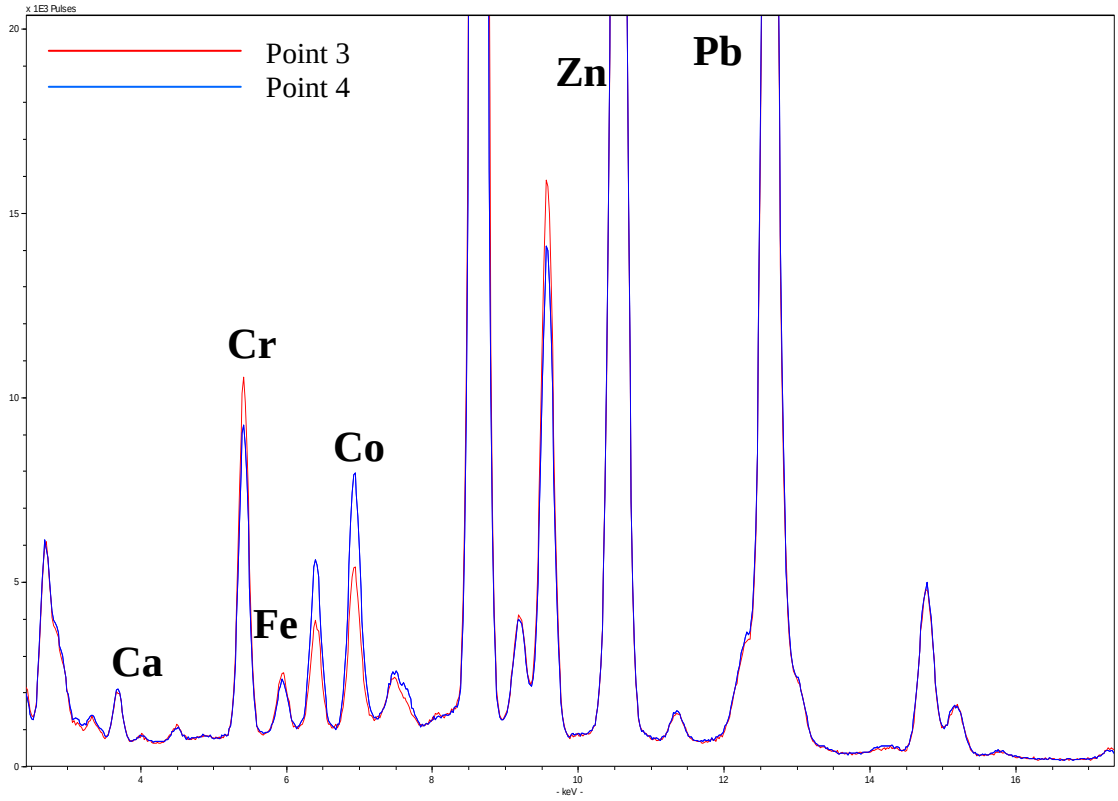

Figure 63. *Afternoon Back of Laurel Heights.* Point 3, the green of the grass and point 4, the signature.

Evening in the Bluebonnets

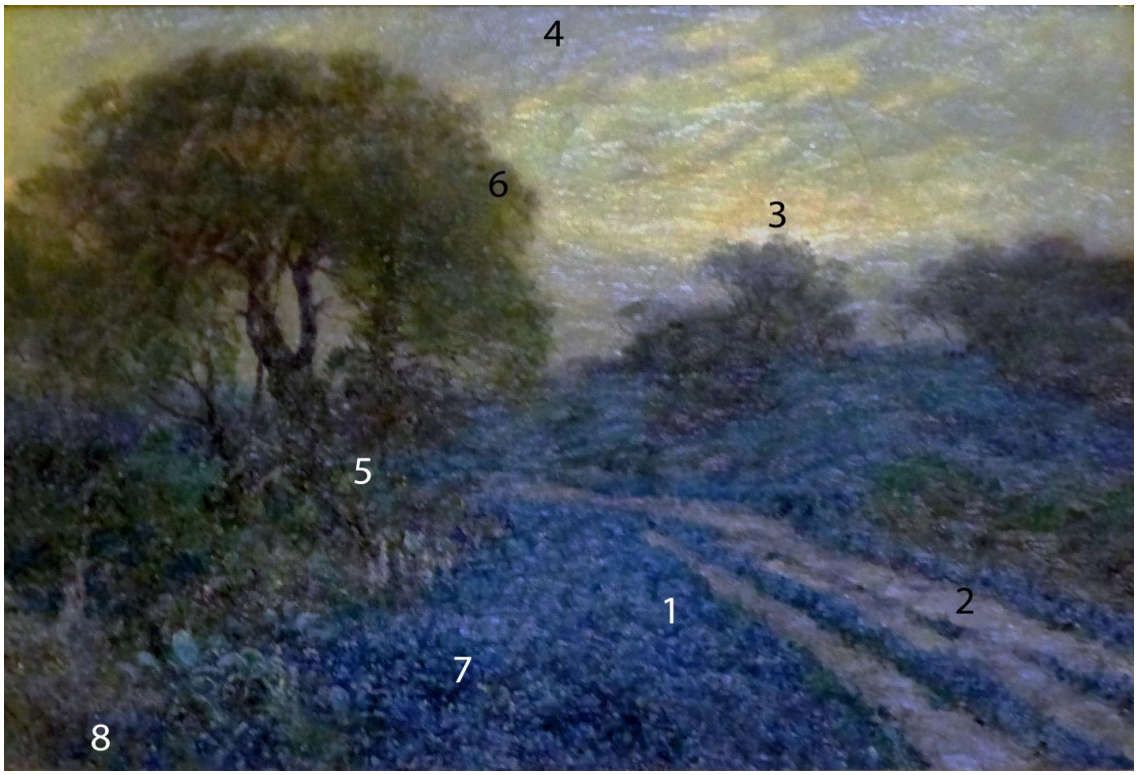

Figure 64. *Evening in the Bluebonnets*. 1914, signed Julian Onderdonk, Oil on Canvas, 12in x 16in, Villa Finale, San Antonio, TX.

A total of eight points were analyzed for *Evening in the Bluebonnets* (figure 64). Points 1, 2, 4, and 7 are various hues of blue, point 3 is the white in the sky, point 6 is the green of the tree, point 5 is the black of the tree trunk, and point 8 is the signature. The lead in this painting is minute compared to the previous paintings analyzed, and in point 3 it is hardly visible at all. This indicates that the use of lead was not as a white but another color, and the primer for this painting was likely a zinc white.

Blue

Points 1 and 7, the darkest and richest of the blues are notably high in cobalt and tin (figure 65). All four points with the blues have these two elements present, and this indicates that the primary blue utilized in this painting is cerulean blue (CoO SnO_2). Point 2, the lighter blue of the road, has similar peaks for iron and zinc, but lower energy peaks for cobalt and tin. This indicates that the roadway was more heavily mixed with iron based red and zinc white. Point 4, the light blue of the sky, is even more heavily mixed with iron and zinc, and interestingly has the lowest energy lead peak of any of the blues, and the lowest of any point except for point 3, the white.

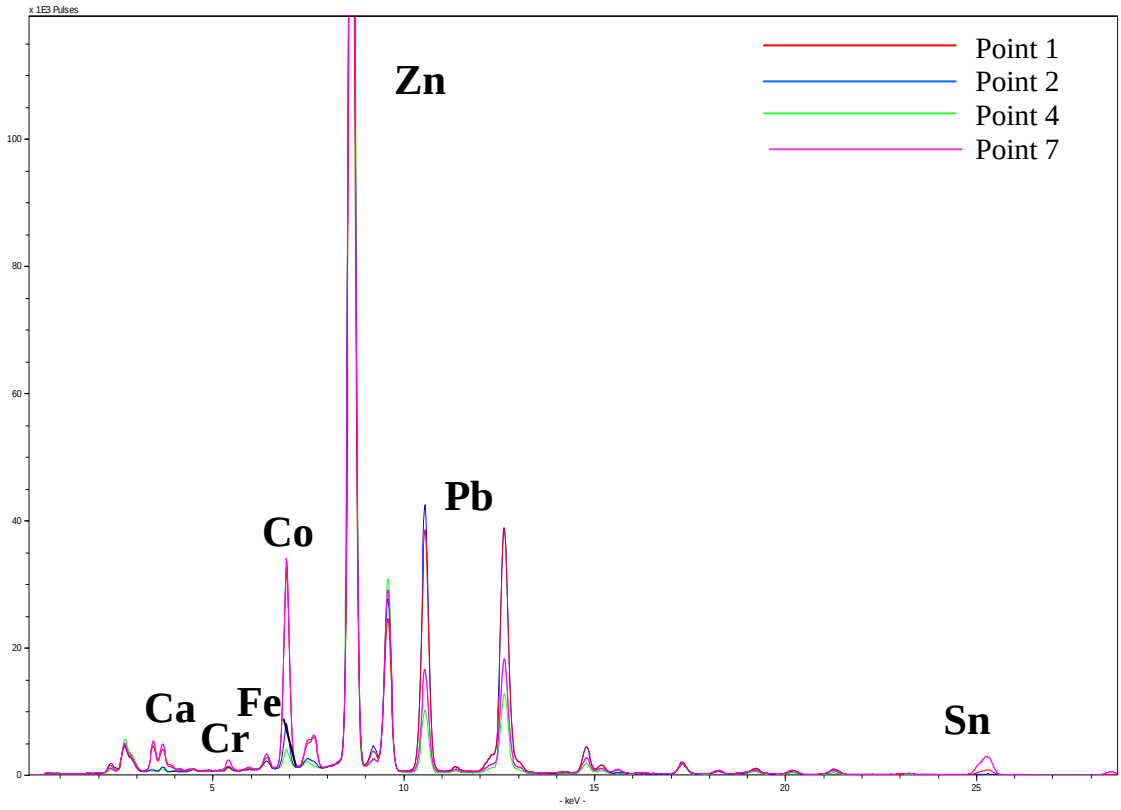

Figure 65. *Evening in the Bluebonnets*. Points 1 and 7, dark blues, points 2 and 4, light blue.

White

Across the eight points analyzed for this painting, zinc is the only pigment which is consistent across all of them, spiking the highest on the white of point 3 (figure 66). This indicates that a zinc white primer was used in the preparation stage, and also used for the white of the cloud and the lightening of other hues. It is possible that lead white incorporated, but it is more likely that the lead was part of another color, like red lead.

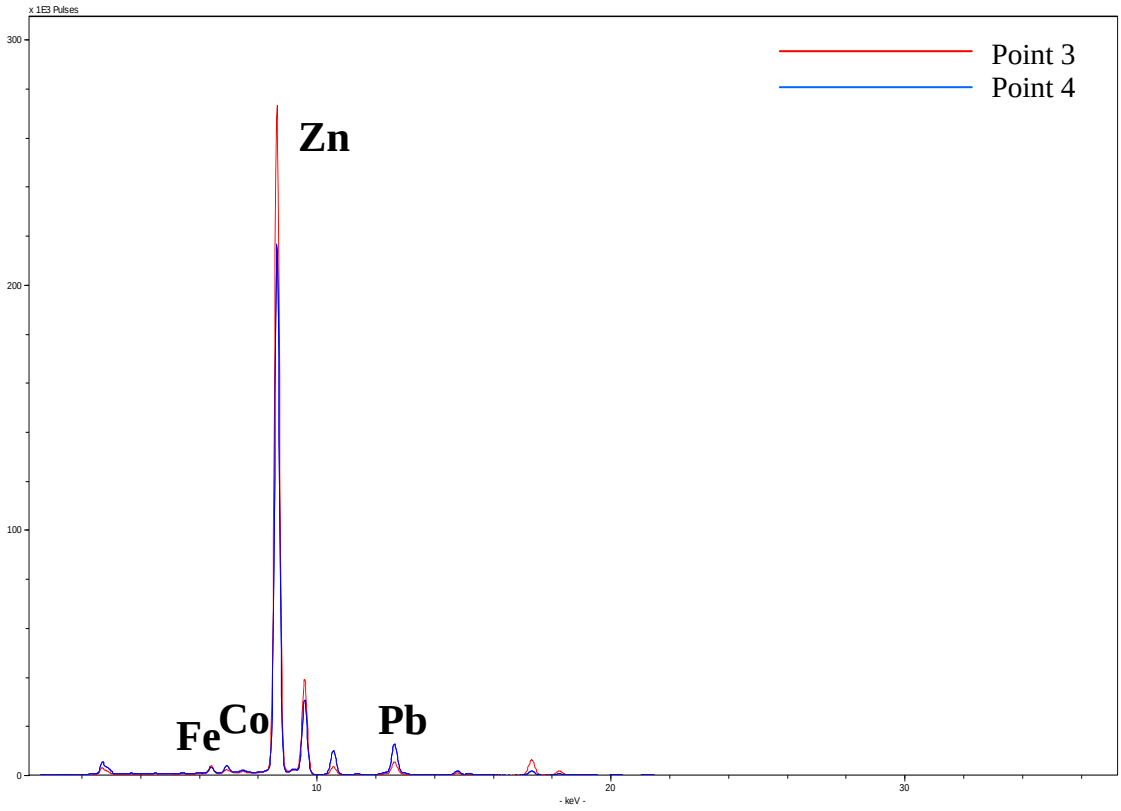

Figure 66. *Evening in the Bluebonnets*. Point 3, white, compared to point 4, light blue.

Green and Black

Compared to the other points, point 6, the green of the leaves in the tree has the highest peak for lead and for chromium (figure 67). The only point with comparable chromium is point 5, the black color of the tree trunk, and there it is obvious that the green of the leaves is present. Point 5 has higher counts for iron and cobalt as well, indicating that the black is a blend of green, an iron based red hematite or ochre or Prussian blue, and the cobalt and tin based cerulean blue.

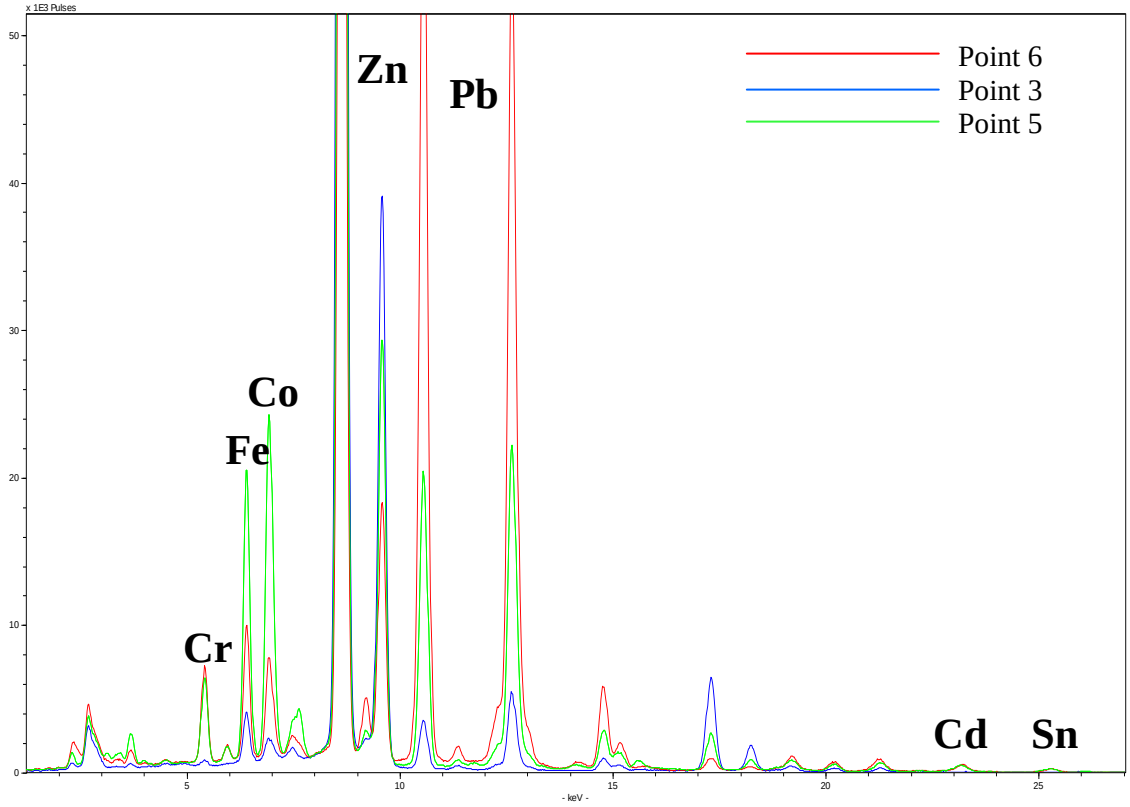

Figure 67. *Evening in the Bluebonnets*. Point 6, green, compared to point 5, black, and point 3, white.

Signature

The signature is very similar in composition to point 5, though it does have a higher peak for lead (figure 68). The black of point 5 has a stronger peak for everything else, indicating a thicker coat of paint.

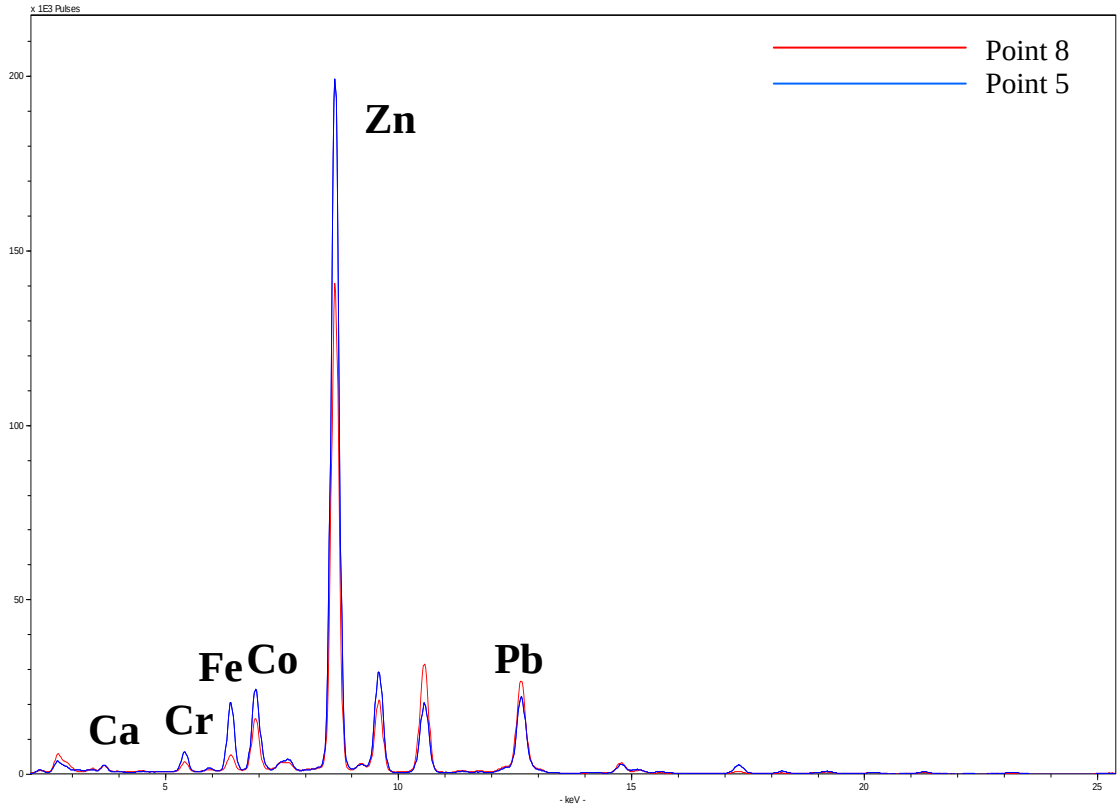

Figure 68. *Evening in the Bluebonnets*. Point 8, the signature, compared to point 5, black.

Texas Mountains on Williams Ranch

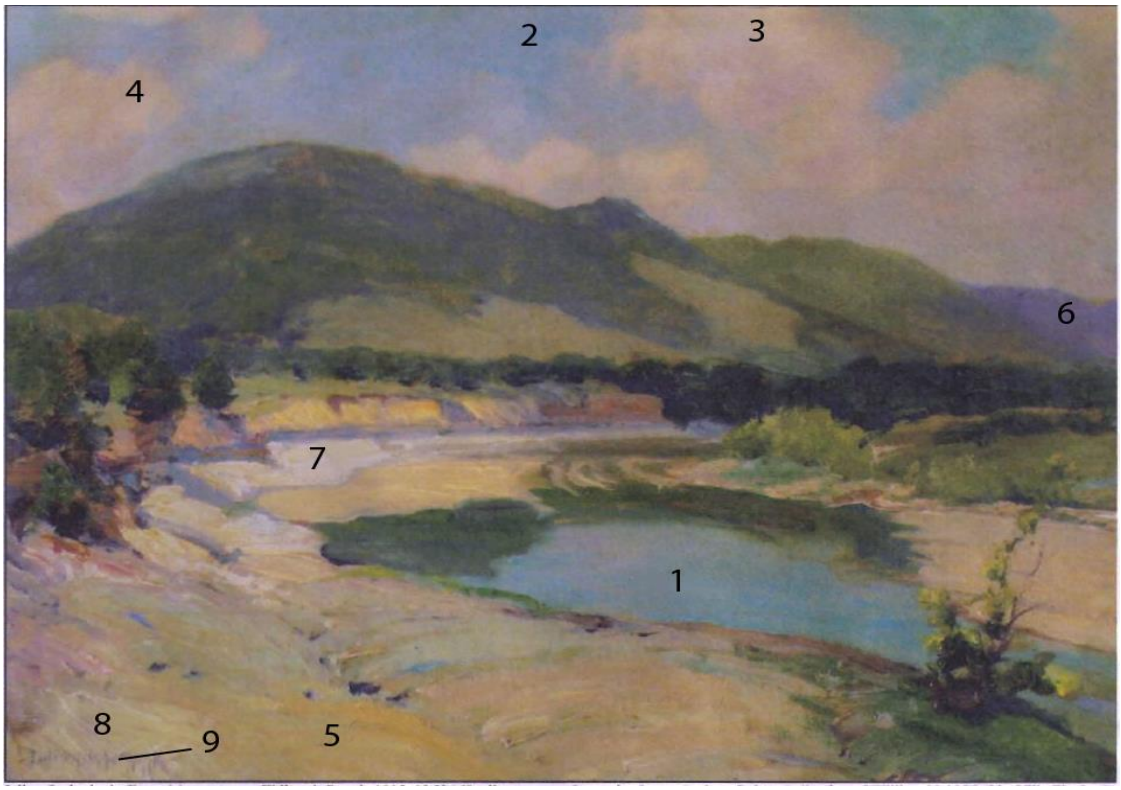

Figure 69. *Texas Mountains on Williams Ranch*. 1915, Onderdonk, Oil on Canvas, 12in x 16in, Villa Finale, San Antonio, TX.

For *Texas Mountains on Williams Ranch* (figure 69), nine points were analyzed. Points 1 and 2 are blues, points 3 and 4 are whites, points 5 and 8 are the yellows of the sand, point 6 is the violet of the mountains that appears to be a mixture of red and blue pigments, point 7 is a mixture of the white, yellow, and the violet, and point 9 is the violet-hued signature. This painting has a titanium peak in point 3, and given that this was painted six to ten years before the production of titanium white for paints, it almost certainly indicates a repair or restoration attempt made since.

Blue

Points 1 and 2 are the blues of the water and the sky, respectively. Both points, like every other point sampled in this painting have a very high peak for zinc, indicating a zinc primer and a zinc white (figure 70). Point 2, which has a slighter redder tint over point 1 has a higher lead signature. This, along with the spectra for points 5 and 7, suggests the use of minium, or red lead (Pb_3O_4). The blue itself is characterized by a peak for cobalt and tin, pointing towards cerulean blue.

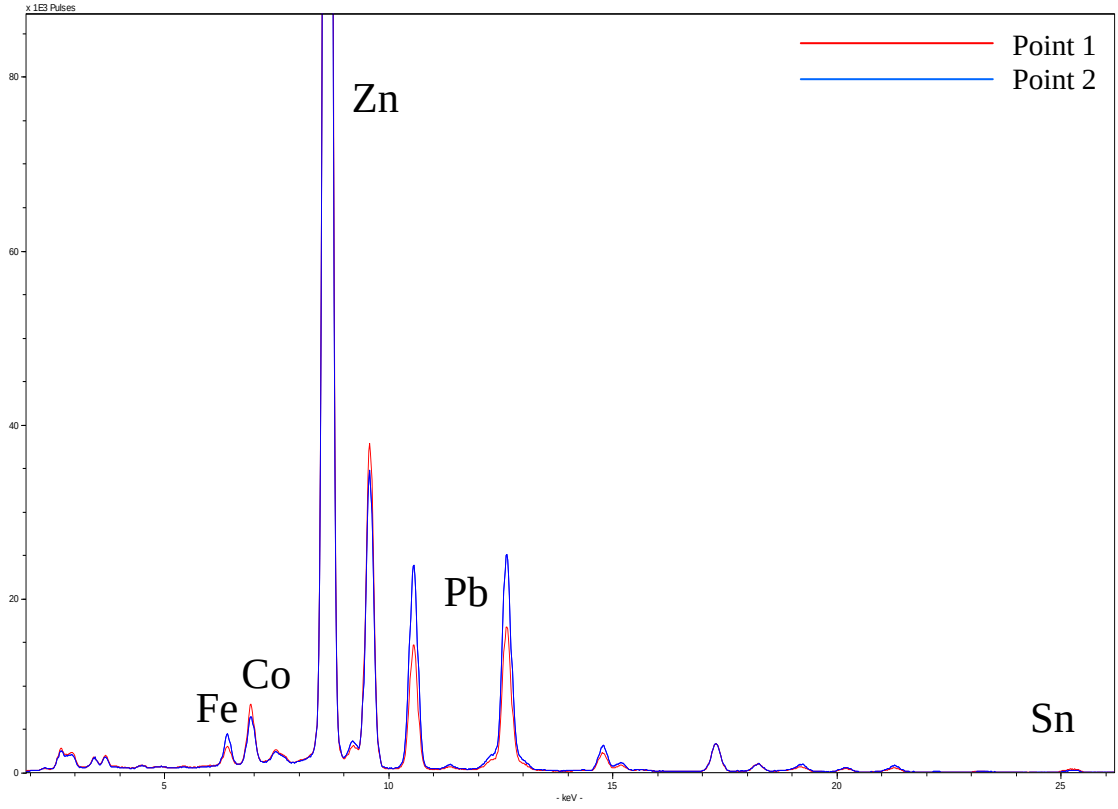

Figure 70. *Texas Mountains on Williams Ranch*. Points 1 and 2, blues.

White

The white, as mentioned above is predominately zinc white. Point 4 has a higher level of lead which might indicate the use of lead white, but there is also a reddish hue to that cloud, further substantiating the use of red lead. Point 3 has a peak for titanium (figure 71). Titanium white was not found in artists pallets until the mid-1920's (Eastaugh et al. 2008, 370), and so this likely represents an area of repair or restoration.

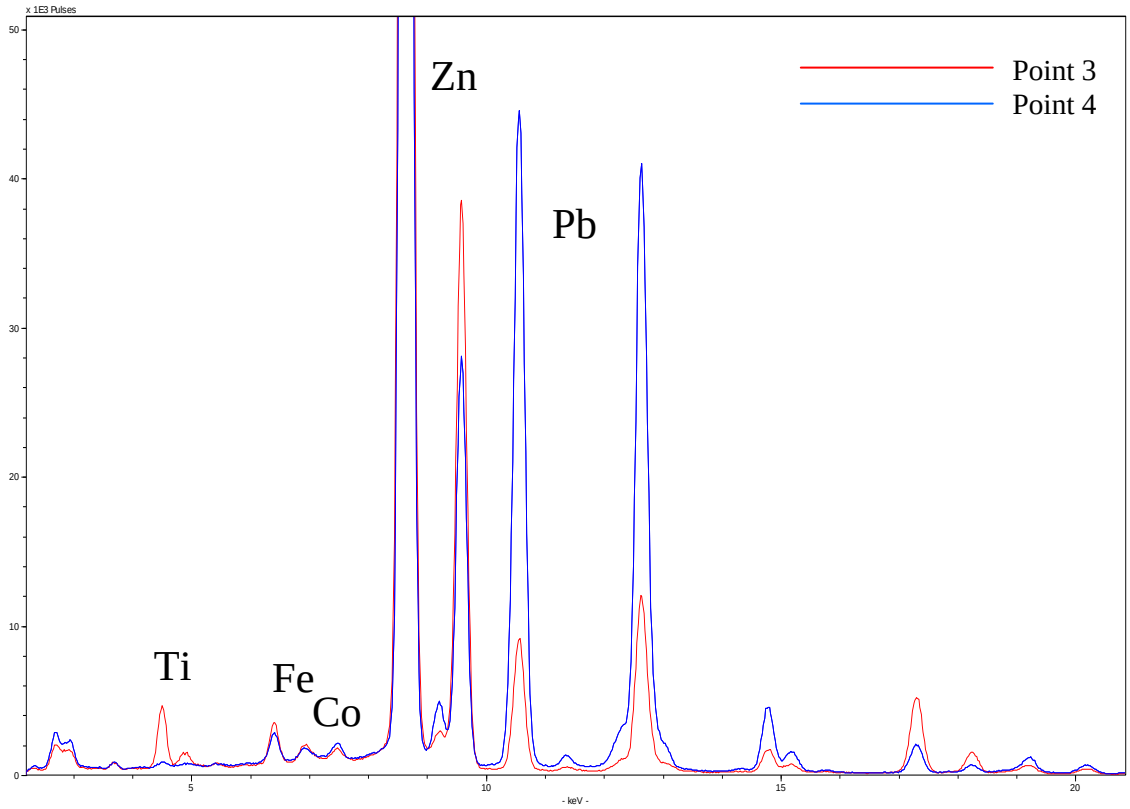

Figure 71. *Texas Mountains on Williams Ranch*. Points 3 and 4, whites.

Yellow

Points 5 and 7 are the both hues of a yellow or beige. Point 5 contains a lead peak and point 7 does not, again indicating a lead red based minium. Point 5 also has a stronger iron peak, indicating either a hematite red or an ochre variant (figure 72). As expected given its brightness, point 7 has a higher peak for zinc, and both points contain cadmium and sulfur, indicative of cadmium yellow.

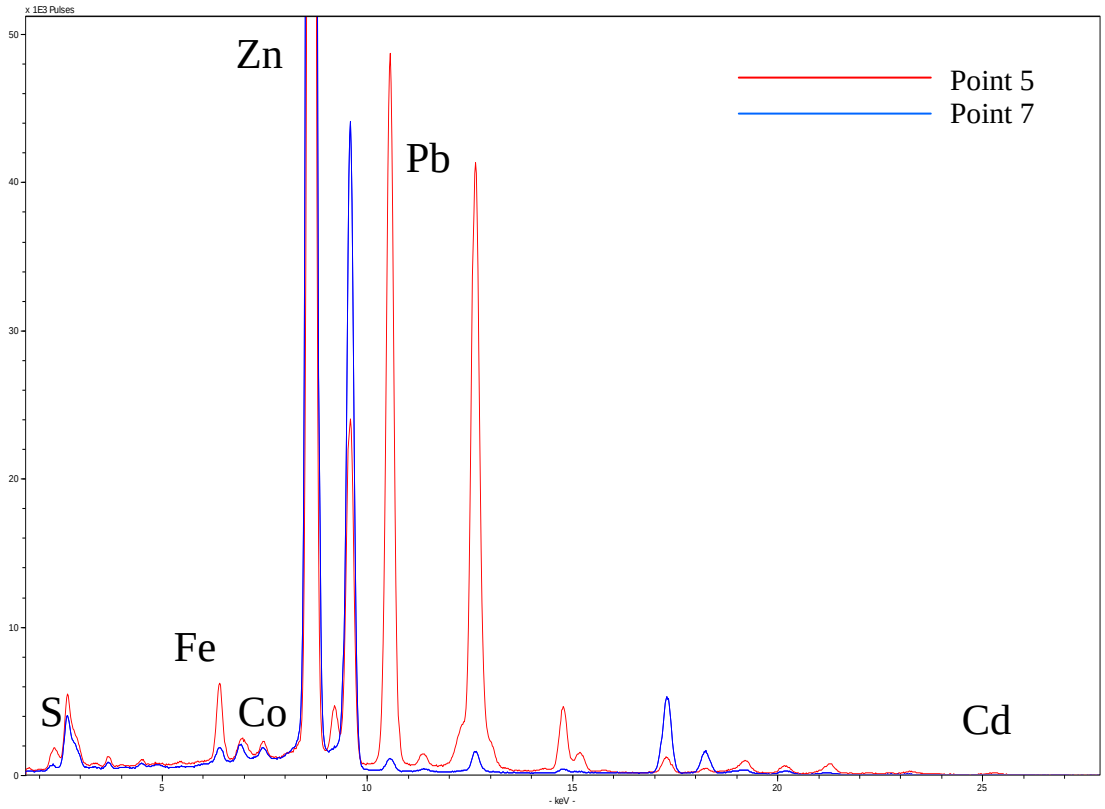

Figure 72. *Texas Mountains on Williams Ranch*. Points 5 and 7, yellows.

Violet

Comparing point 6, the violet of the mountain to point 2, the blue of the sky, the most noticeable difference is the lead peak. Point 6 has a higher level of lead, indicating that the blue was mixed with red lead to achieve the violet hue. Point 2 has a higher peak for cobalt, likely because it is not mixed with the red lead (figure 73).

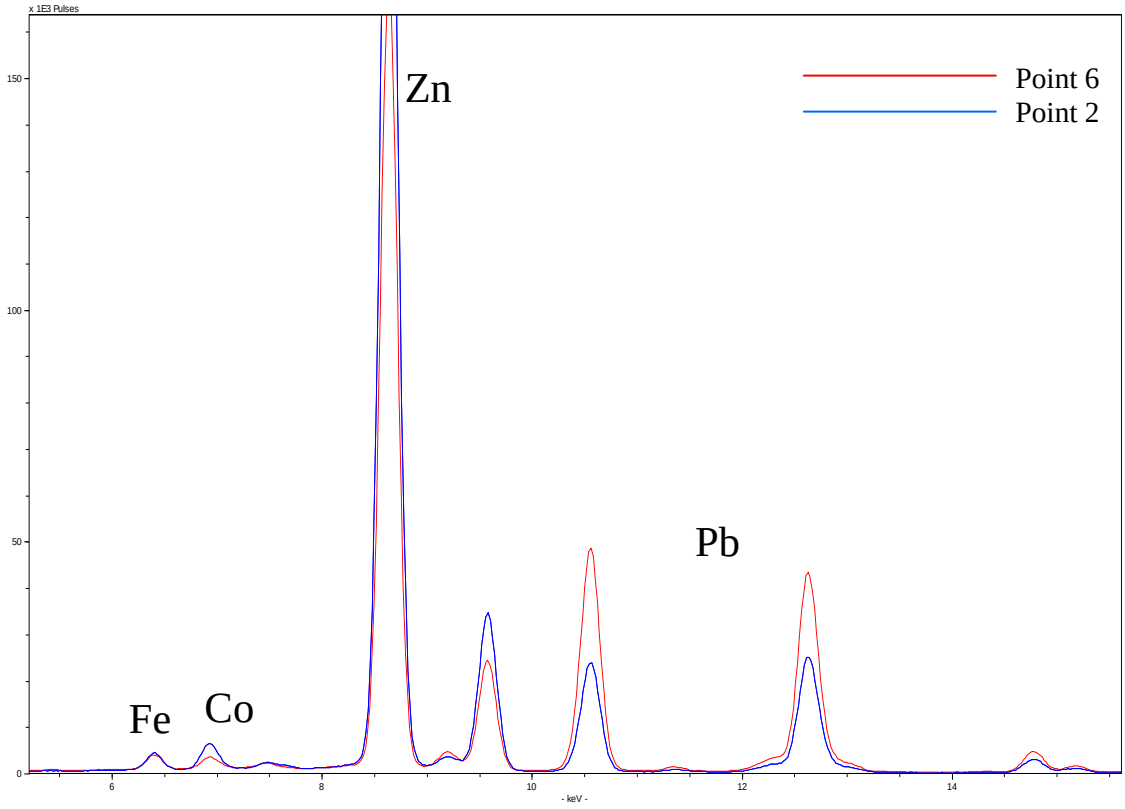

Figure 73. *Texas Mountains on Williams Ranch*. Point 6, violet, compared to point 2, blue.

Signature

Point 8, the background, and point 9, the signature, are nearly identical except for the signature having a higher peak for lead (figure 74). Again, this indicates the use of red lead.

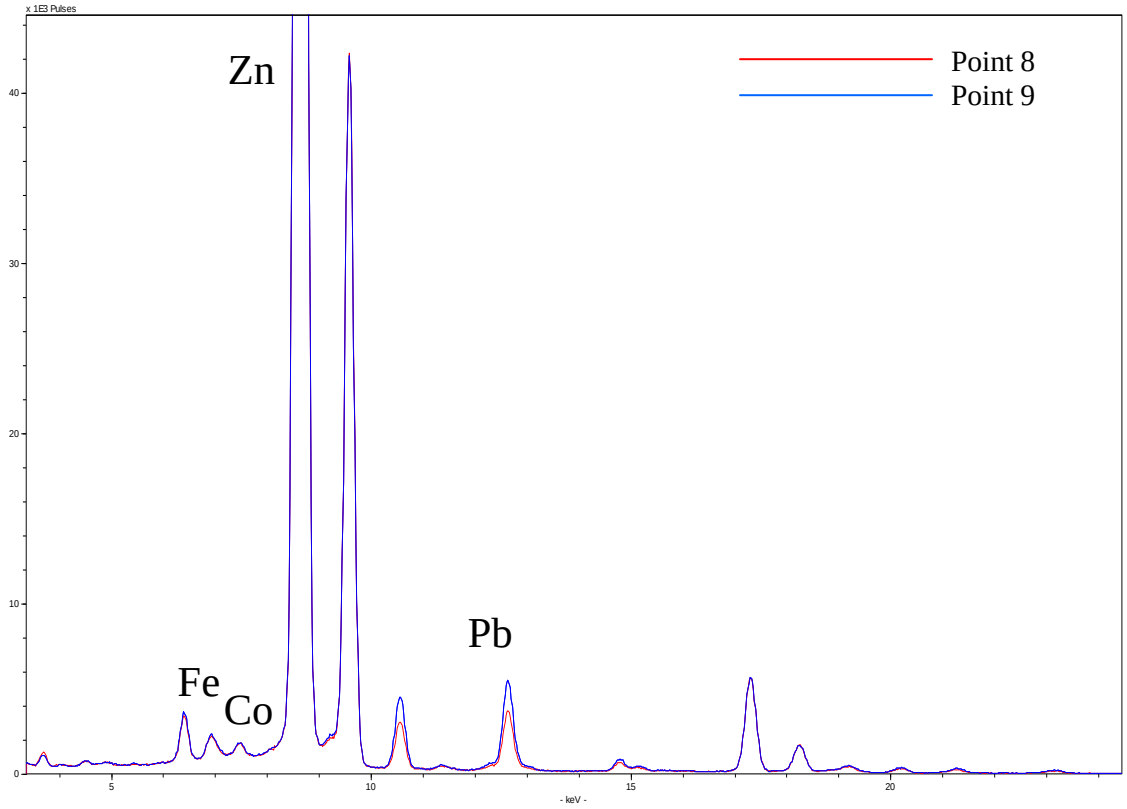

Figure 74. *Texas Mountains on Williams Ranch*. Point 8, the background, and point 9, the signature.

Williams Ranch, 20 West of Kerrville TX, near Junction

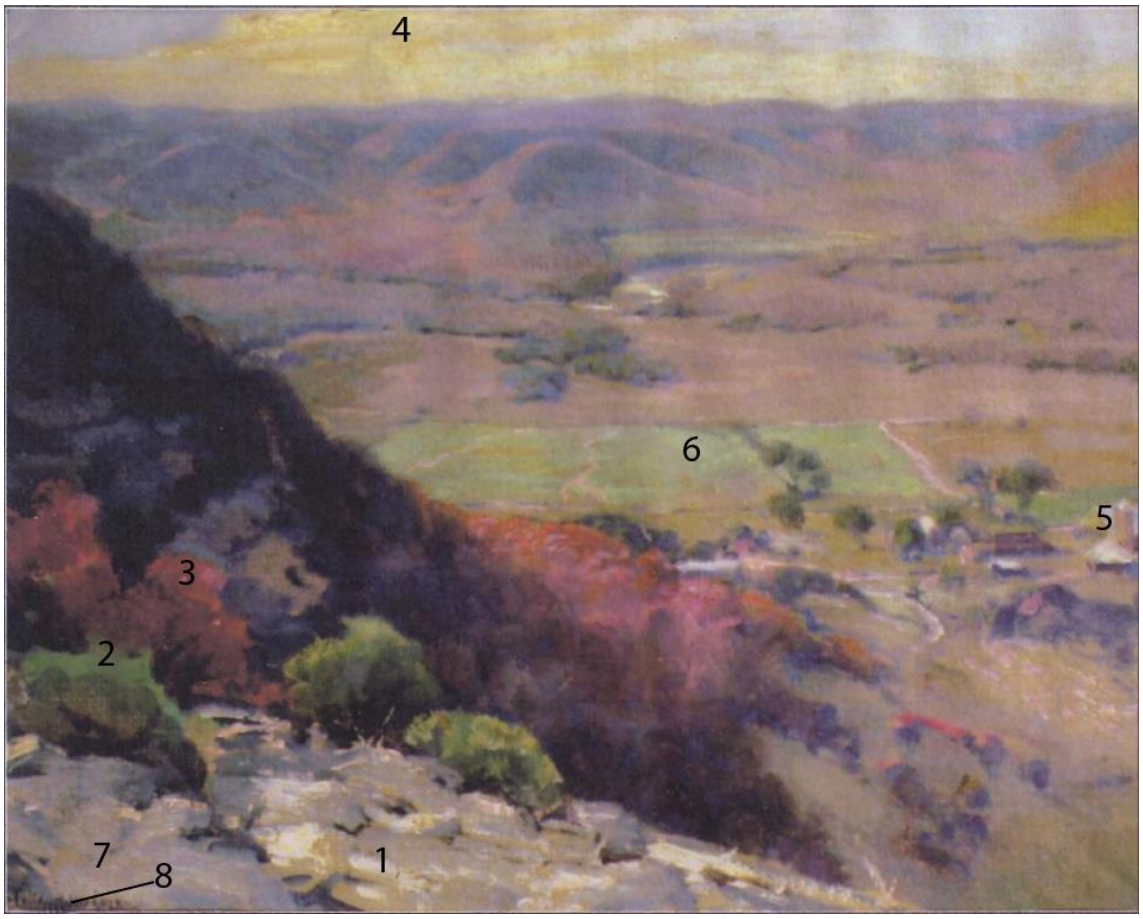

Figure 75. *Williams Ranch, 20 West of Kerrville TX, near Junction*. 1915, Signed Julian Onderdonk, Oil on Canvas Board, 8in x 10in, Villa Finale, San Antonio, TX.

A total of eight points were analyzed on *Williams Ranch* (figure 75). Points 1, 4, and 5 are white highlights, points 2 and 6 are greens, point 3 is the red of the bush, point 7 is the background of the rock and point 8 is the signature.

White

Points 1, 4, and 5 are the white highlights on the rock, the sky, and on the house to the right of the painting. Point 1 has a slightly larger peak for zinc, and point 5 has a slightly larger peak for lead (figure 76). Apart from these two elements, there is very little of note here. By process of elimination, the zinc is almost certainly zinc white. Point 5 has a peak for chromium, which could indicate zinc yellow, but the presence of the nearby green is a likely source for chromium, and the lack of chromium in the lighter yellowish-white of point 4 means that this is most likely a zinc white with some iron based ochre added to tint it.

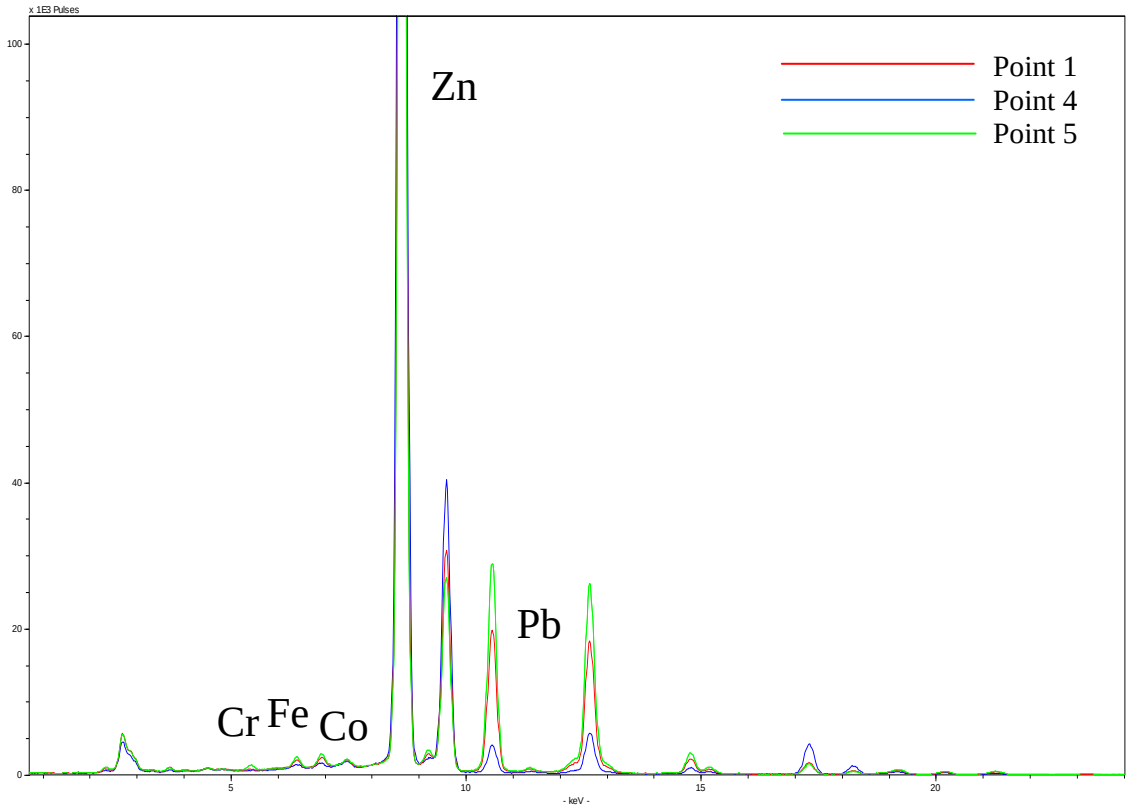

Figure 76. *Williams Ranch, 20 West of Kerrville TX, near Junction*. Points 1, 4, and 5, whites.

Green and Yellow

The most notable element in the greens of points 2 and 6 is chromium, indicating that the green is chromium dioxide (figure 77). Points 2 and 6 also have a peak for cadmium, which is more than likely from cadmium yellow.

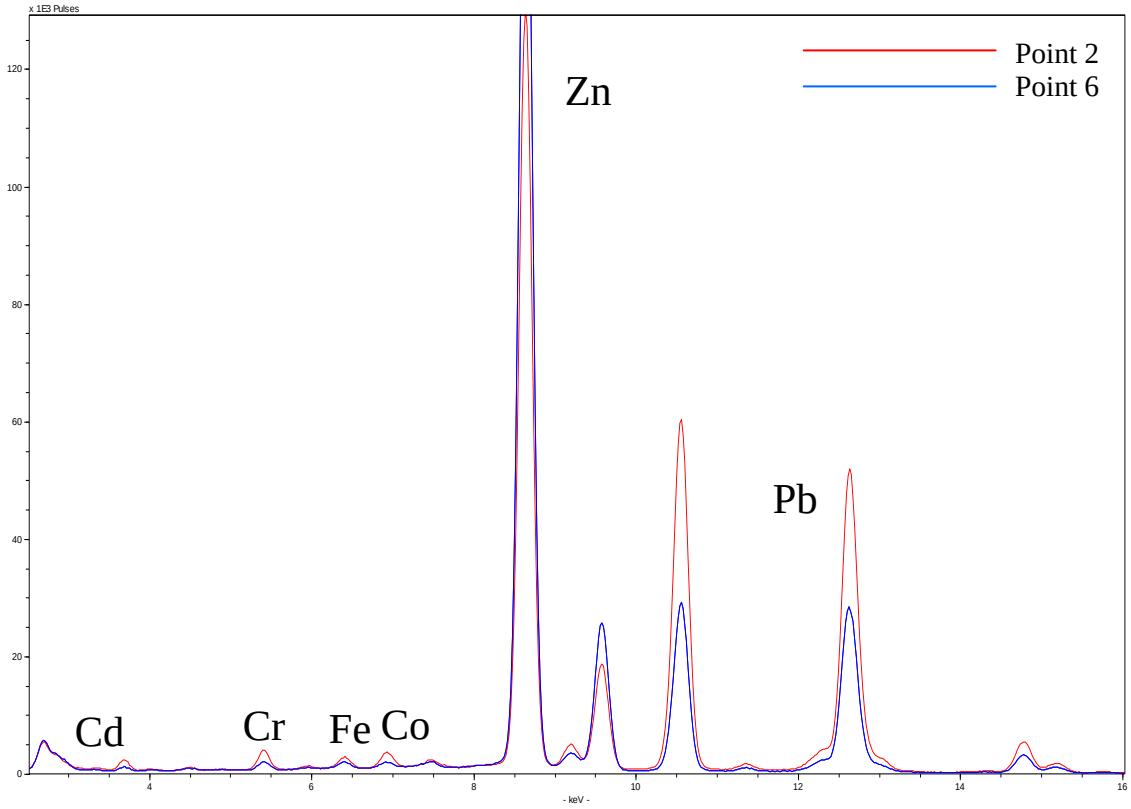

Figure 77. *Williams Ranch, 20 West of Kerrville TX, near Junction*. Points 2 and 6, greens.

Red

Point 3, the red of the bush, has the strongest iron peak of any of the points analyzed (figure 78). This points to the use of a hematite red or red ochre. The reddish hue in the white of point 5 when compared to point 1, and the higher presence of lead in the signature over the background likely indicates the use of red lead as well.

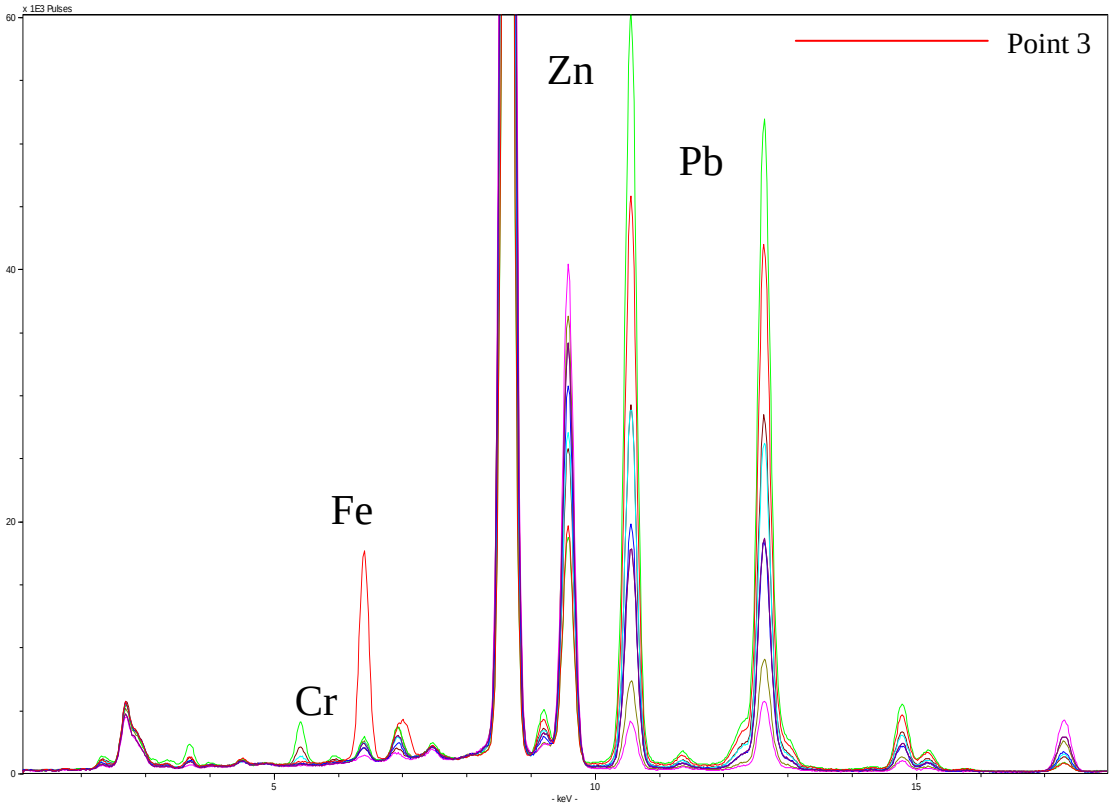

Figure 78. *Williams Ranch, 20 West of Kerrville TX, near Junction*. Point 3, red, compared to the rest of the points.

Signature

Comparing points 7 and 8, the only element where the peak is higher in the signature than the background is lead (figure 79). As mentioned above, this probably points to the use of red lead, also known as minium.

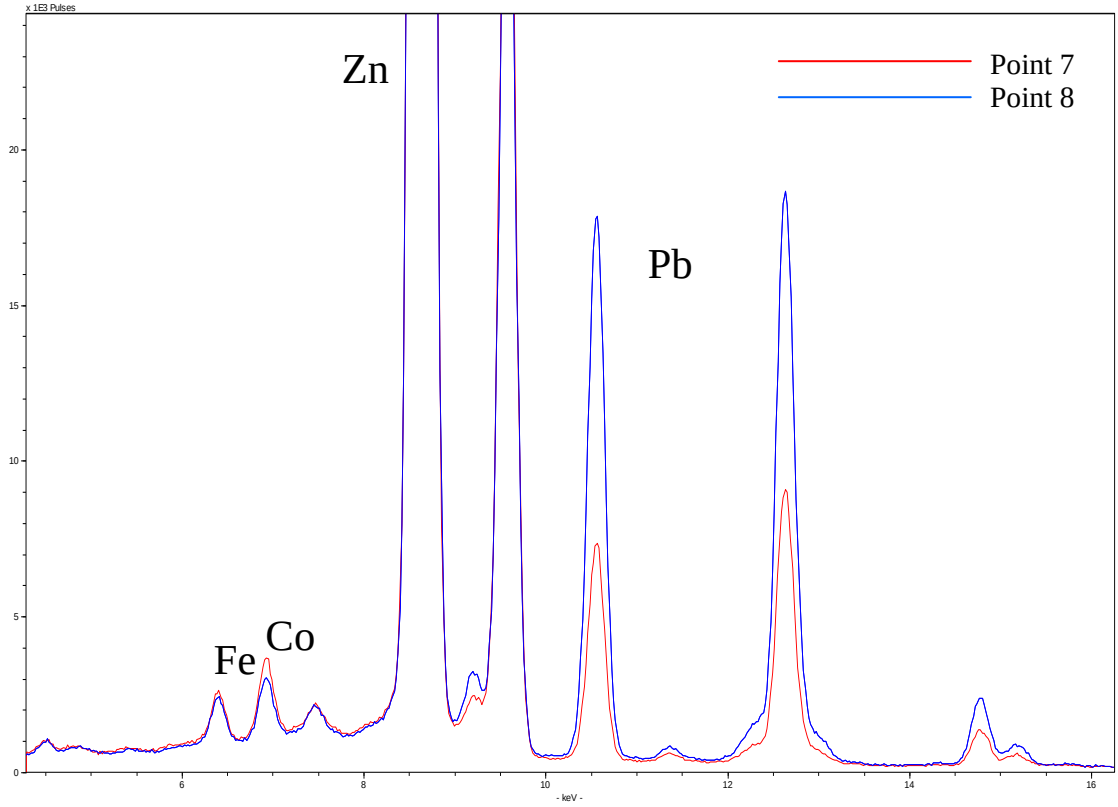

Figure 79. *Williams Ranch, 20 West of Kerrville TX, near Junction*. Point 7, the background, and point 8, the signature.

Late Afternoon Sunlight on the Bluebonnets

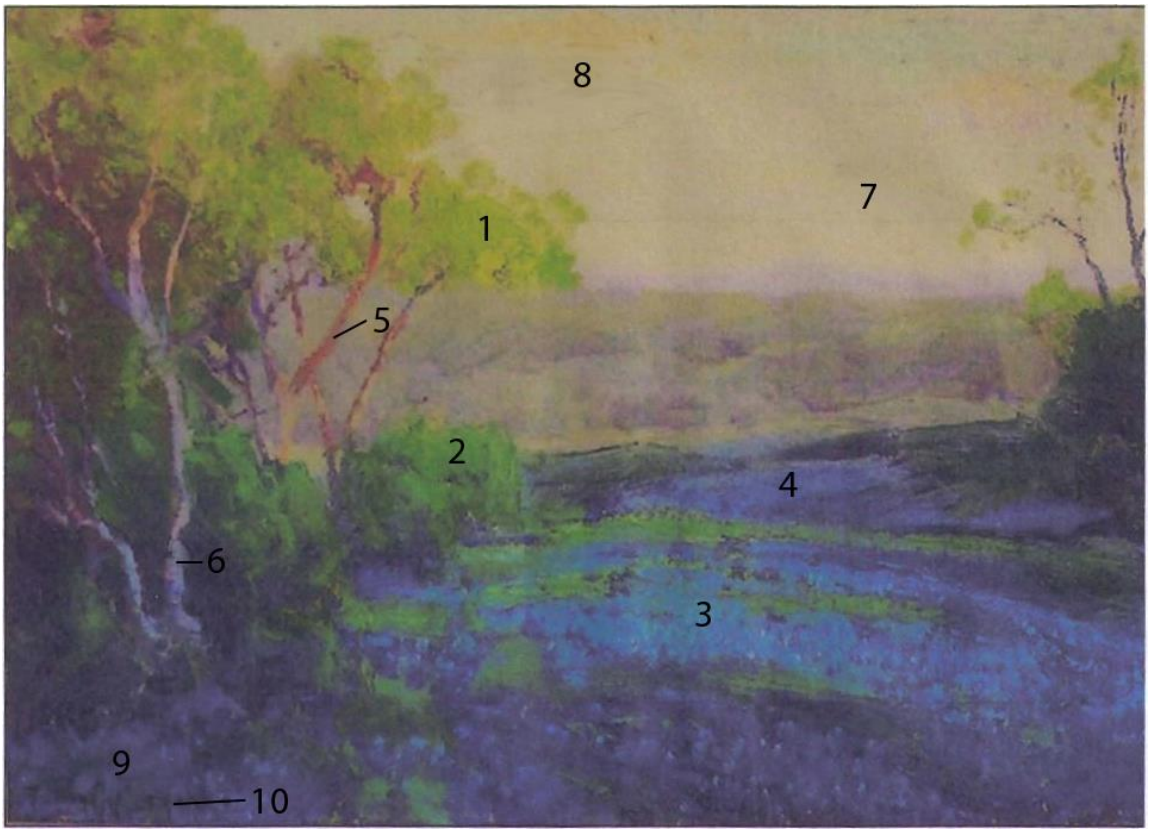

Figure 80. *Late Afternoon Sunlight on the Bluebonnets*. 1916, Signed Julian Onderdonk, Oil on Board, 6in x 9in, Witte Museum, San Antonio, TX.

A total of ten points were analyzed for *Late Afternoon Sunlight on the Bluebonnets* (figure 80). Points 1 and 2 are the different hues of green, points 3 and 4 are the blues, point 5 is the red of a tree trunk, point 6 is the violet of a tree trunk, points 7 and 8 are the whites of the sky (the picture above looks more yellow than the painting does in life). The painting has strong zinc peaks in each point, indicating that it was primed with a zinc white primer.

Green

Points 1 and 2 are light and dark green, and both have a strong peak for chromium (figure 81). Point 1 has a strong peak for cobalt and iron, and when compared to the blues and reds, appears to be a blend from these pigments. Point 2 has a higher cadmium peak, indicating that the lighter shade of green is mixed with cadmium yellow.

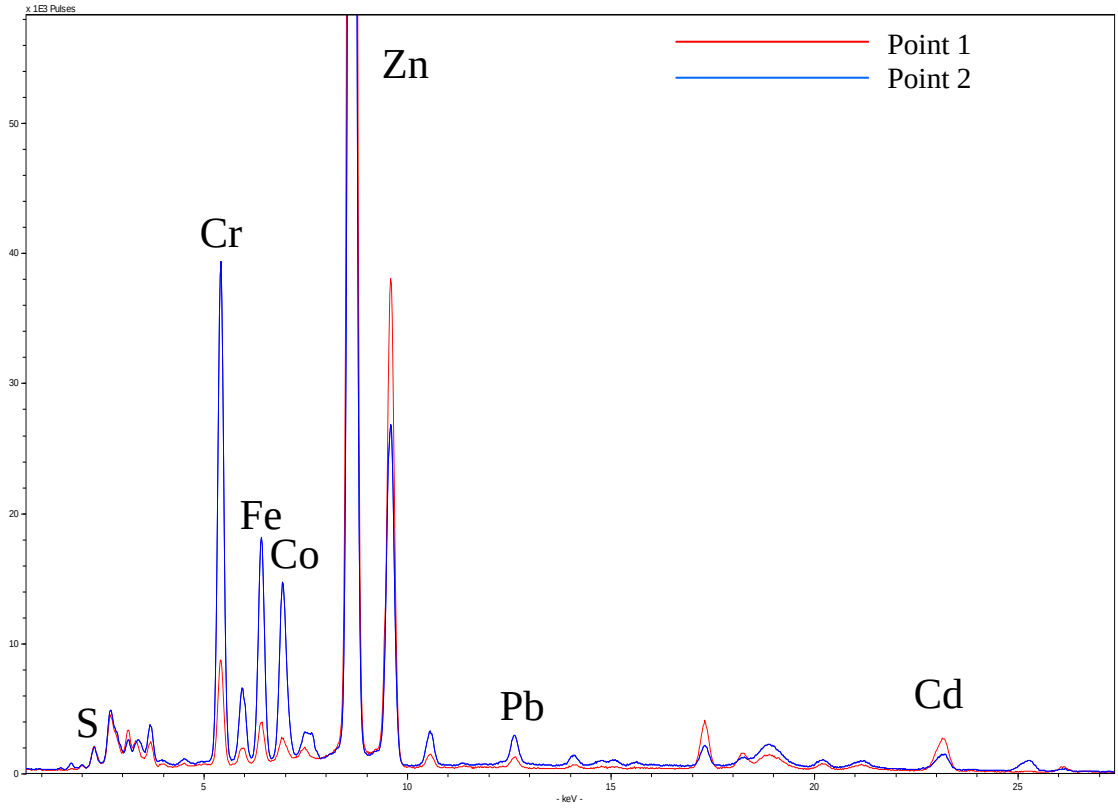

Figure 81. *Late Afternoon Sunlight on the Bluebonnets*. Points 1 and 2, greens.

Blue

Points 3 and 4 are each a different hue of the bluebonnets. Point 3, the lighter blue, has a slightly higher peak for cobalt and tin, though it is clear that both of these points are cerulean blue (figure 82). Point 4 has a strong peak for chromium, indicating chromium green was used to darken the blue.

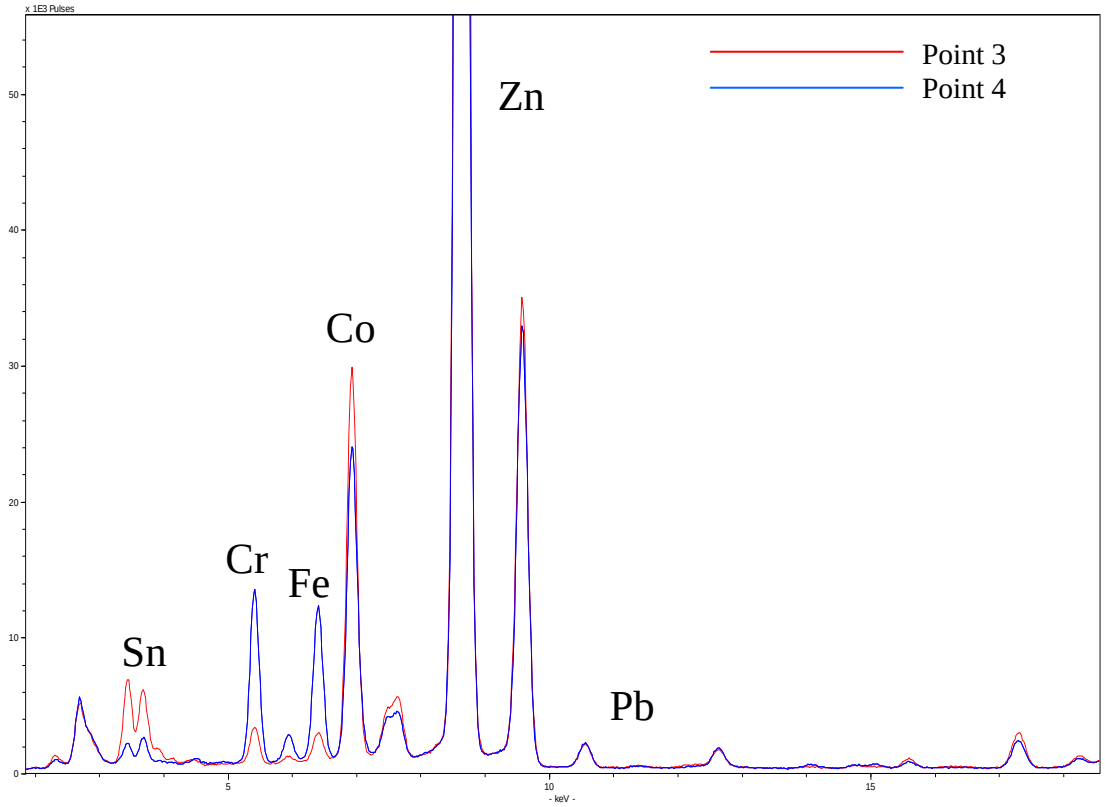

Figure 82. *Late Afternoon Sunlight on the Bluebonnets*. Points 3 and 4, blues.

Red and Violet

Point 5, the red of the tree branch is a mixture of cobalt, iron, zinc, and cadmium. The most likely candidate for red in this group is the iron, either as ochre or a hematite. Comparing the red, the blue of point 3, and the violet of point 6, the violet appears to be a mixture of cerulean blue and the iron red, with a strong peak for the chromium green as well (figure 83). The chromium green likely indicates that the tree trunk was painted over the green of the leaves.

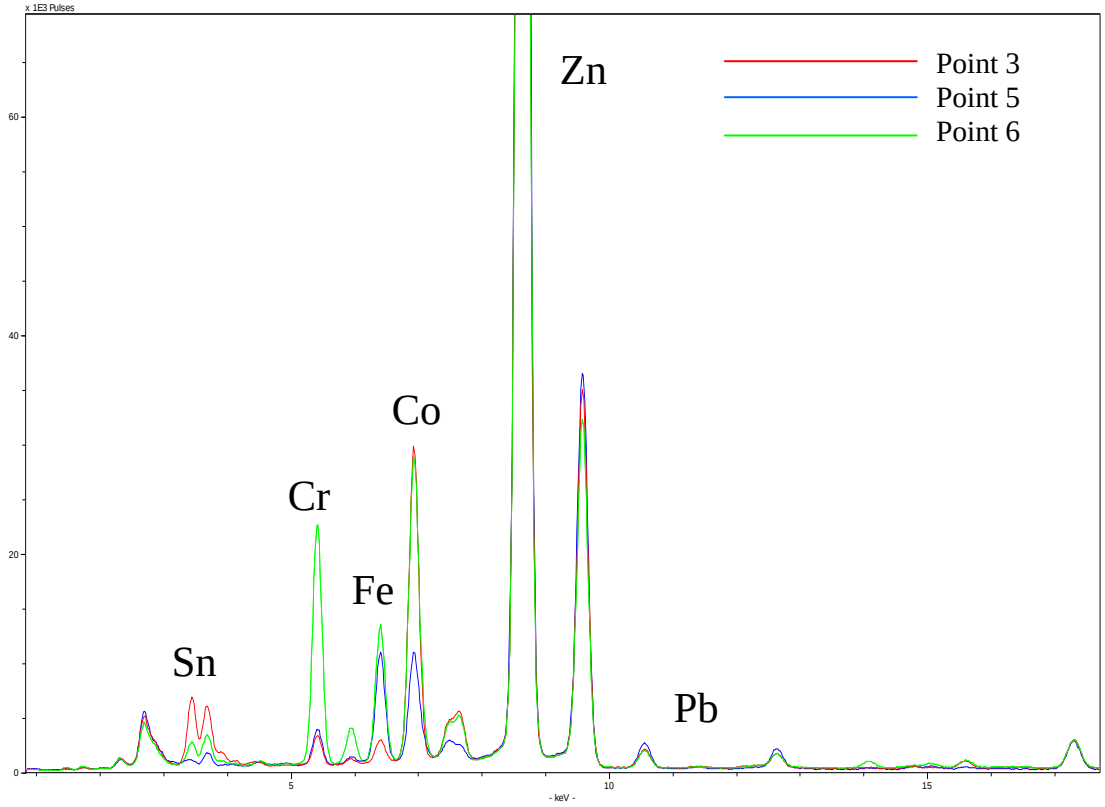

Figure 83. *Late Afternoon Sunlight on the Bluebonnets*. Point 3, the blue, compared to point 5, red, and point 6, violet.

White

The whites of peaks 7 and 8 are very distinctly zinc white (figure 84). There are no other elements of note in these points.

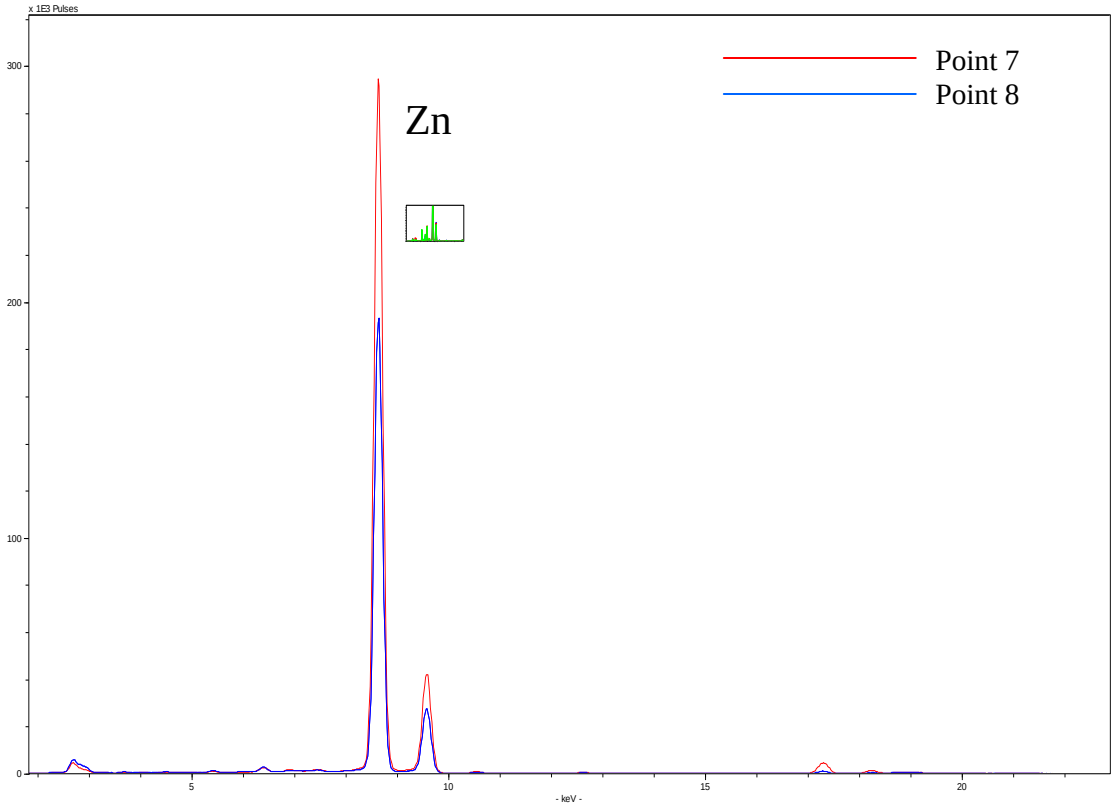

Figure 84. *Late Afternoon Sunlight on the Bluebonnets*. Points 7 and 8, whites.

Signature

Point 9, the dark violet background of the signature and point 10, the signature itself are very similar in their spectral profile. Point 9 has a higher peak for zinc and cobalt, and point 10 has a higher peak for iron and chromium (figure 85). This indicates that the signature is a mixture of green and red to create the brown of the letters.

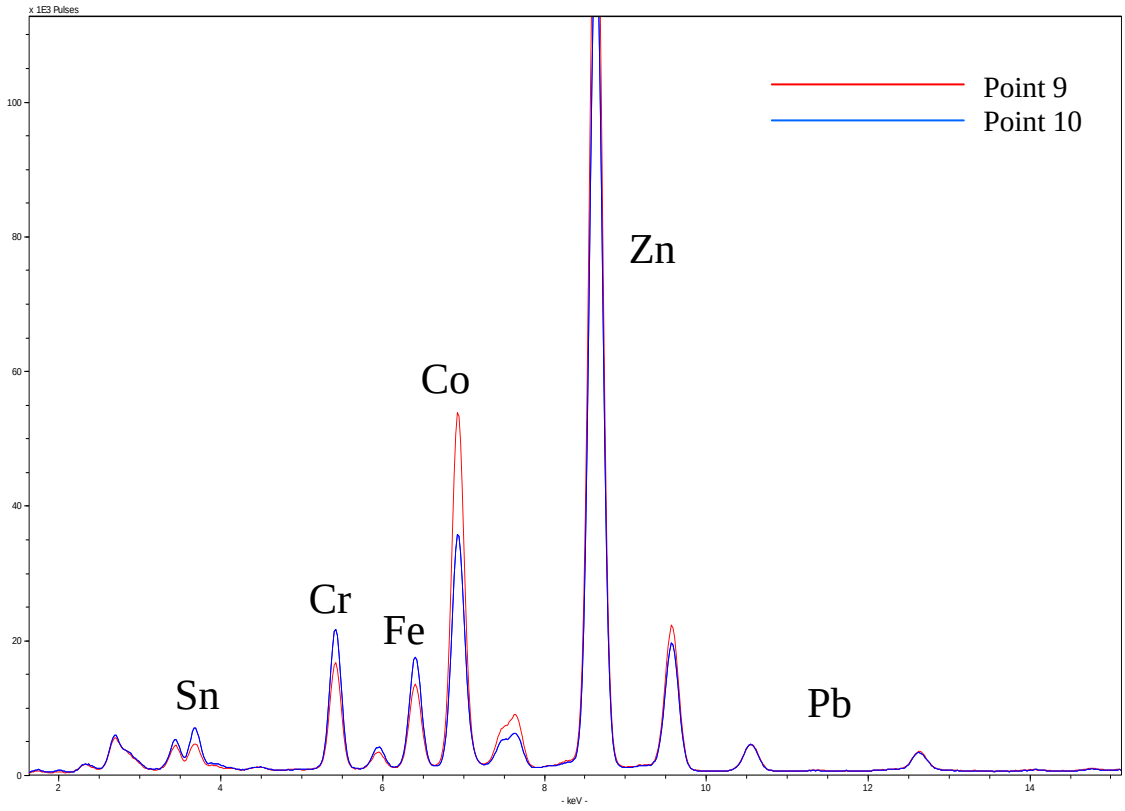

Figure 85. *Late Afternoon Sunlight on the Bluebonnets*. Point 9, the background, compared to point 10, the signature.

Milkweed in Bandera

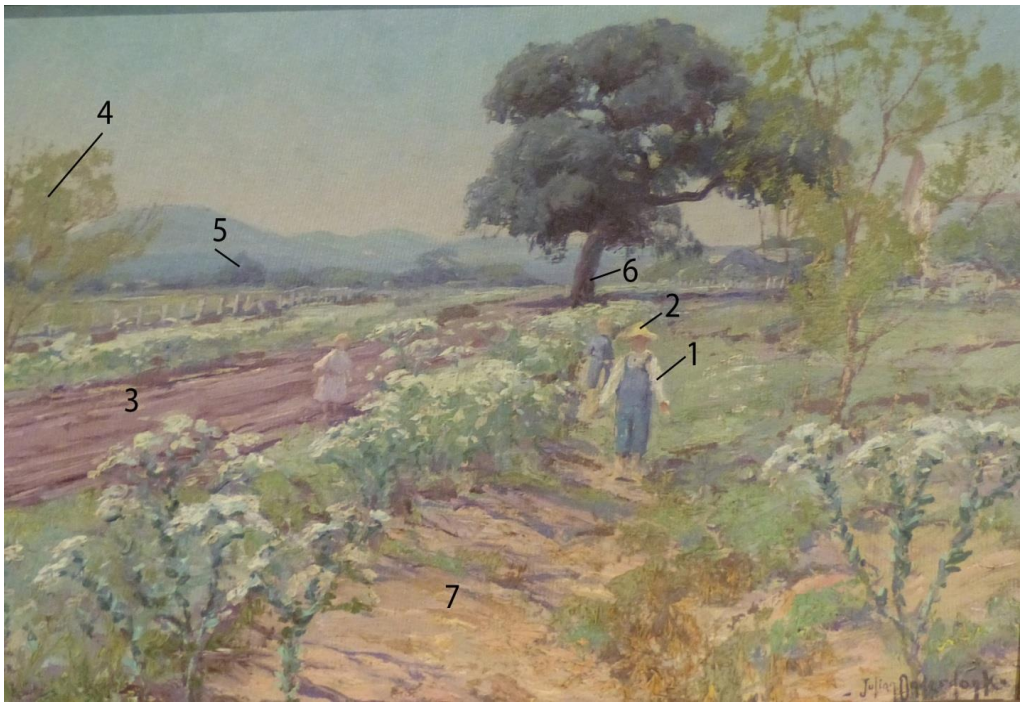

Figure 86. *Milkweed in Bandera*. 1916, Signed Julian Onderdonk, Oil on Canvas, 12in x 16in, Witte Museum, San Antonio, TX.

A total of seven points were analyzed for *Milkweed in Bandera* (figure 86). Point 1 is white, point 2 is the yellow of the hat, point 3 is the blend of red and white in the road, point 4 is the green of a tree, point 5 is the blue of the mountain in the background, point 6 is the black of the tree trunk, and point 7 is the orange of the ground. This particular painting proved to be the most difficult set of pigments to decipher with the XRF data. The elements that are typical to Onderdonk's work are there, but they do not occur alongside the colors that they have in his other works. The analysis is presented below, but will be excluded from the collection wide analysis because of a lack of

reliable data. Future testing will need to be done to establish the pigments used in this painting.

White

Zinc and lead are present in every point, but the zinc peak levels are more consistent between peaks, suggesting a zinc white primer. The white of the shirt in point 1 has the second highest zinc peak in the painting, suggesting a zinc white paint as well (figure 87).

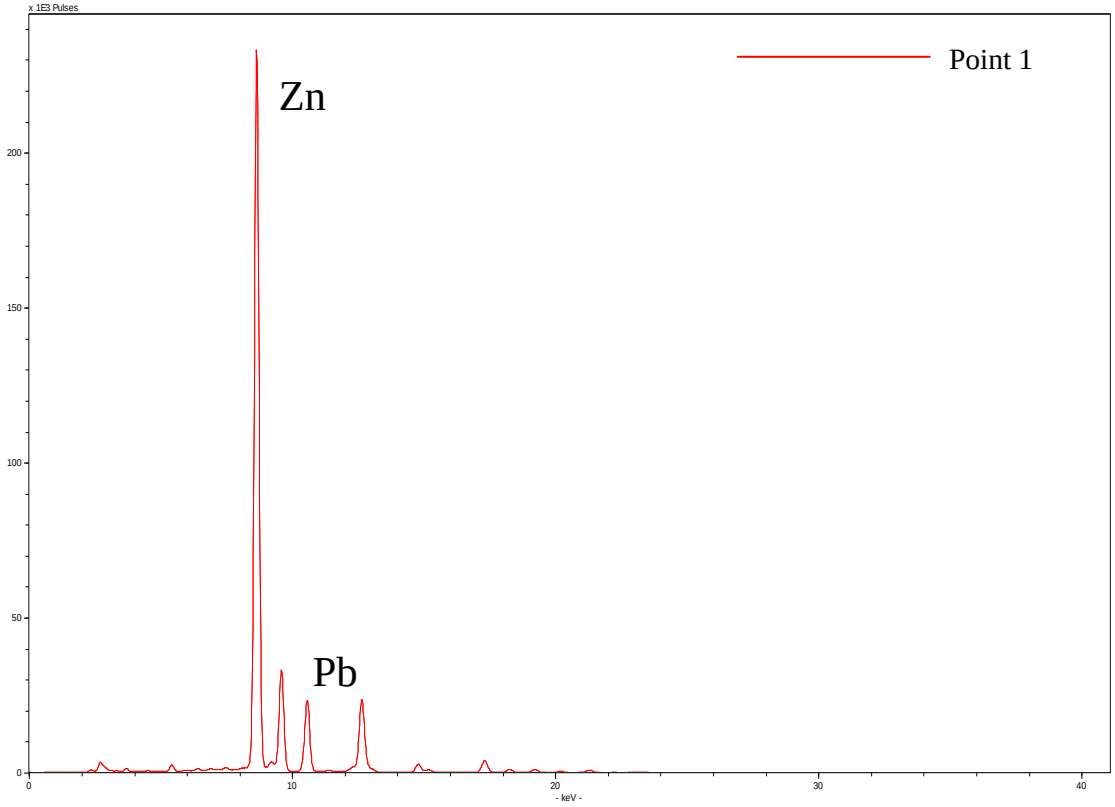

Figure 87. *Milkweed in Bandera*. Point 1, white.

Yellow

The spectrum for the yellow of point 2 is very similar to the white of point 1 (figure 88). The yellow has slightly higher peaks for cadmium, cobalt, sulfur, and lead, indicating the use of cadmium yellow (CdS).

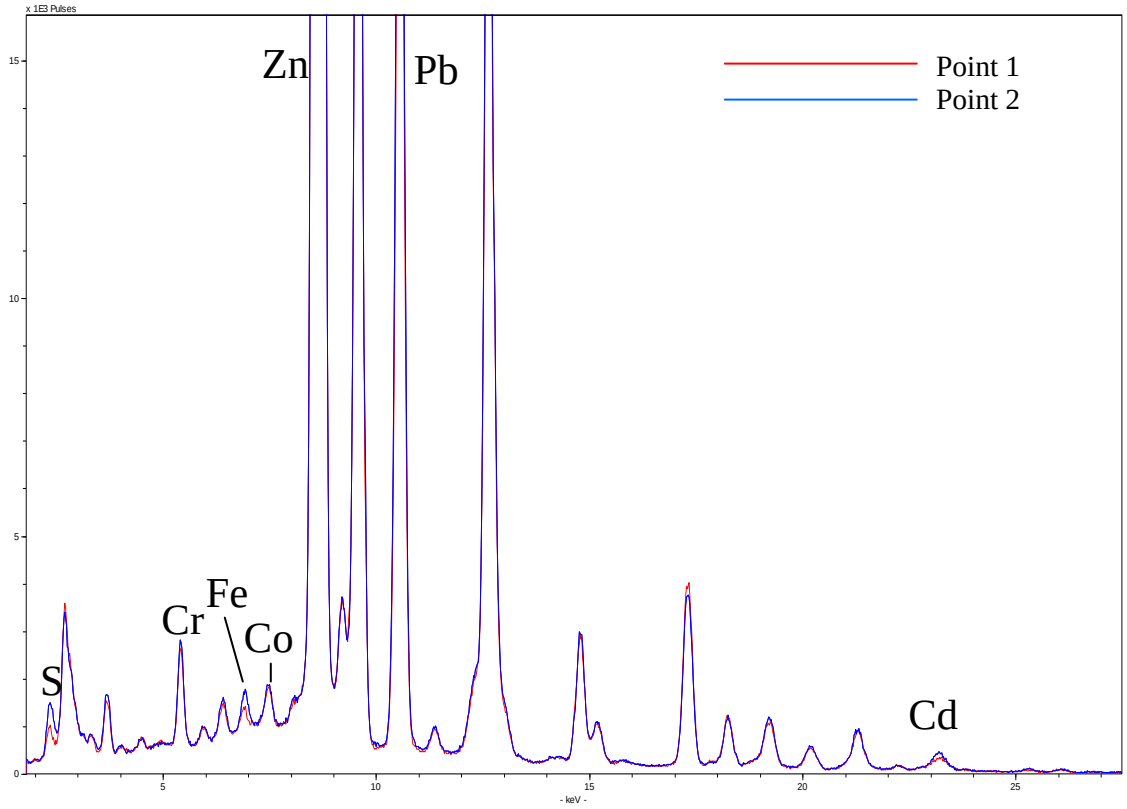

Figure 88. *Milkweed in Bandera*. Point 1, white, compared to point 2, yellow.

Red, Orange, and Black

Point 3, the analysis of the red in the road does not seem to have any characteristic peaks that can be definitively associated with a red pigment. Compared to the white of point 1, the only peak in point 3 that does not occur is copper (figure 89). There are no red pigments that are synthesized from copper, only blues and greens, and therefore the most likely explanation initially points toward an organic red pigment like madder ($C_{14}H_8O_4$). The black for point 6, which is also a strong candidate for having some red pigment in it, has a slightly elevated iron peak compared to the red and the white, though not substantially different enough to identify the red as iron based. Likewise, the lead levels are too consistent between all the points to attribute the lead to a red pigment. The black of point 6 has the highest peaks of all six for cadmium, chromium and copper, which are either blues, yellows, or greens. The orange of point 7 contains mercury, which is only used for red, in the form of vermillion (HgS) (figure 90). The green of point 4 also contains mercury, likely from the tree branch the leaves were painted over. The red then is most likely vermillion, and possibly an organic red as well. This painting would have to be re-analyzed to know for sure whether or not the red in the road is organic based or mercury based.

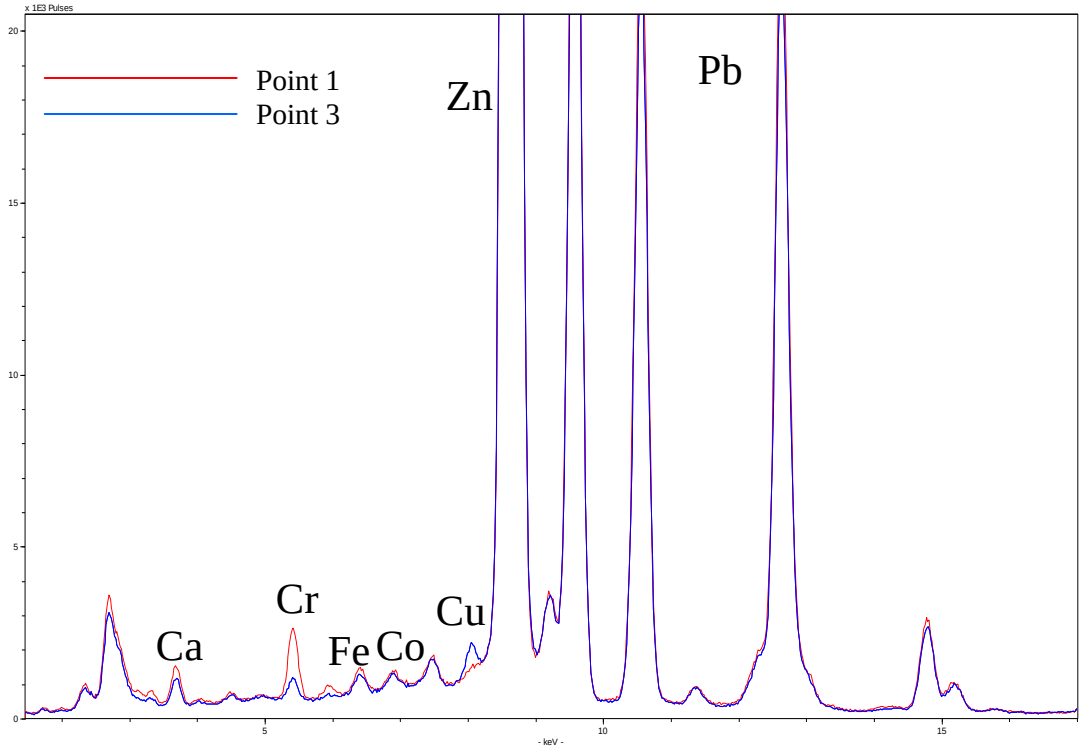

Figure 89. *Milkweed in Bandera*. Point 3, red, compared to point 1, white.

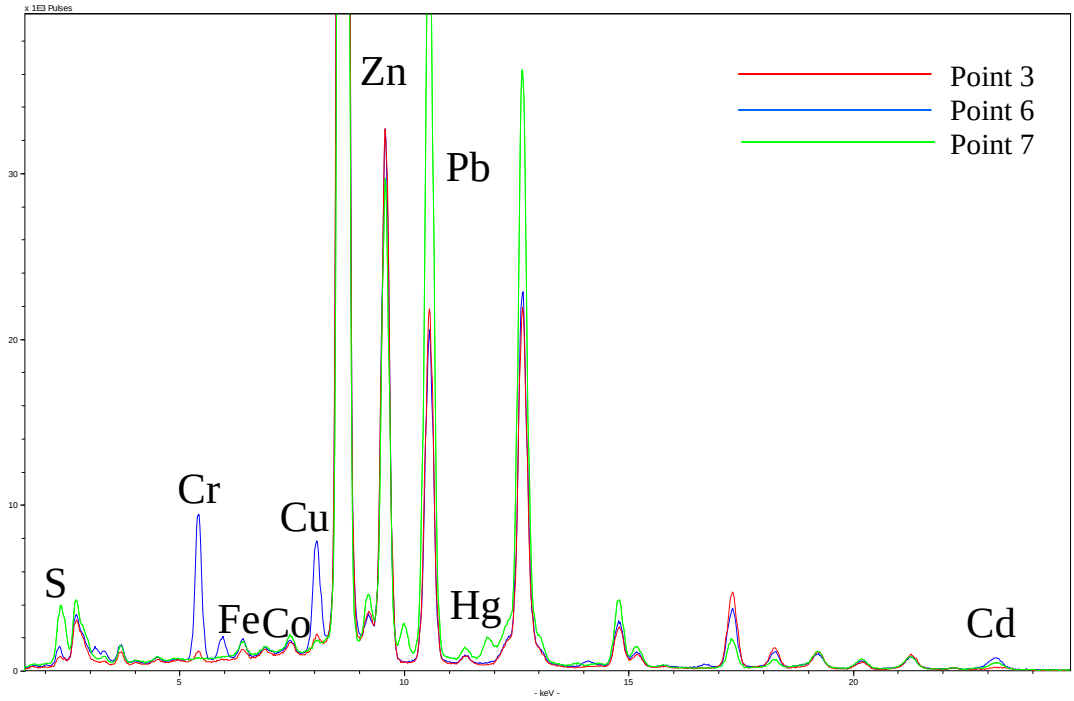

Figure 90. *Milkweed in Bandera*. Point 3, red, compared to point 6, black, and point 7 orange.

Green and Blue

The copper peak in point 5 could be Egyptian blue, though oddly the chemical formula for Egyptian blue, ($CaCuSiO_4$), fits better with the green point than the blue. Comparing point 4, the green, to point 5, the blue, point 4 has a higher peak for sulfur, calcium, copper, mercury, and lead (figure 91). Of these, only copper can be responsible for green pigment, so by the process of elimination, the green is likely either malachite or verdigris, both copper-based green pigments. The only element that has a distinctly higher peak in the blue of point 5 over the green of point 4 is chromium, which also complicates interpretation. Chromium is used primarily in yellows and greens, and so the blue is likely coming from one of the less prominent elemental peaks. Cobalt is initially the obvious choice, and the lack of tin and aluminum suggests smalt, a ground cobalt doped glass. It is possible that this is an organic blue, but given the difficulty of interpreting so much of this painting, it is impossible to say without further testing.

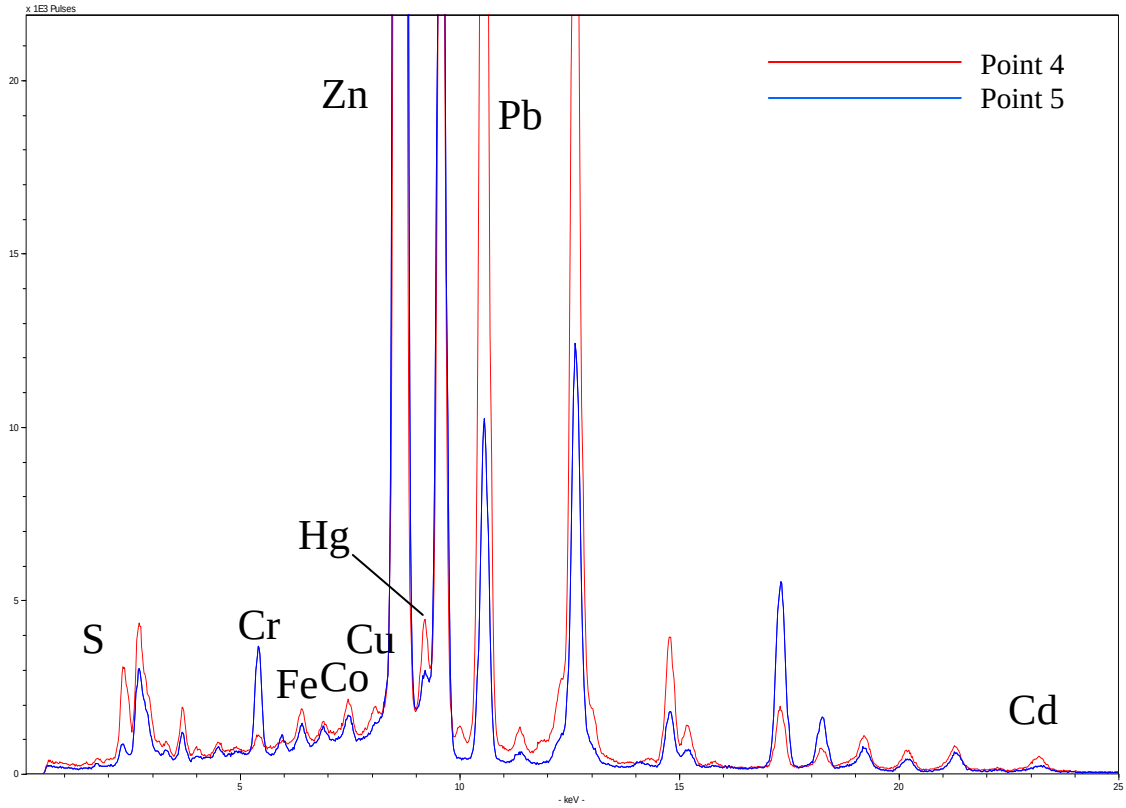

Figure 91. *Milkweed in Bandera.* Point 4, green, compared to point 5, blue.

Bluebonnets at Sunset San Antonio

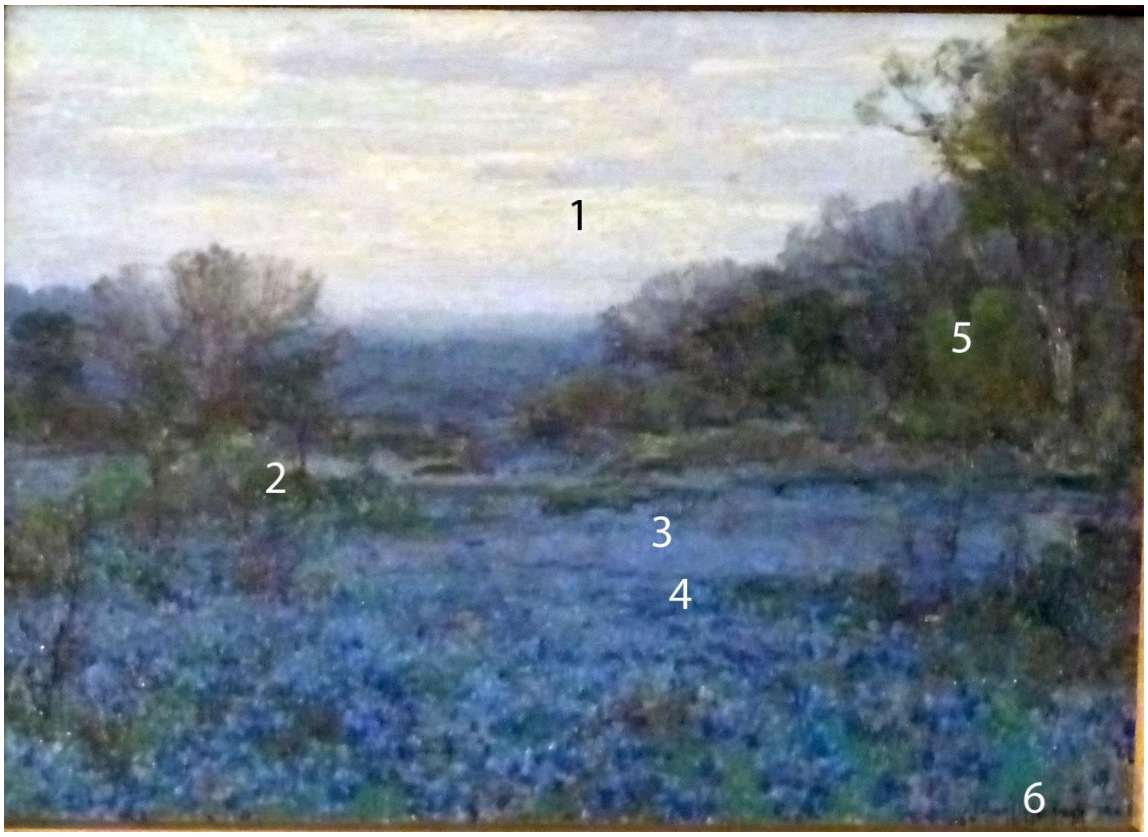

Figure 92. *Bluebonnets at Sunset San Antonio*. 1919-20, Signed Julian Onderdonk, Oil on Board, 9in x 12in, Villa Finale, San Antonio, TX.

A total of six points were analyzed for *Bluebonnets at Sunset San Antonio* (figure 92). Point 1 is the white of the sky, points 2 and 5 are greens of the trees, point 3 and 4 are hues of blue, and point 6 is the signature.

White

The white of the sky, point 1, is primarily a zinc white, with some lead (figure 93). The lead peak for point 1 is the lowest lead peak in the painting, so it is more likely that the white of the clouds is a zinc white.

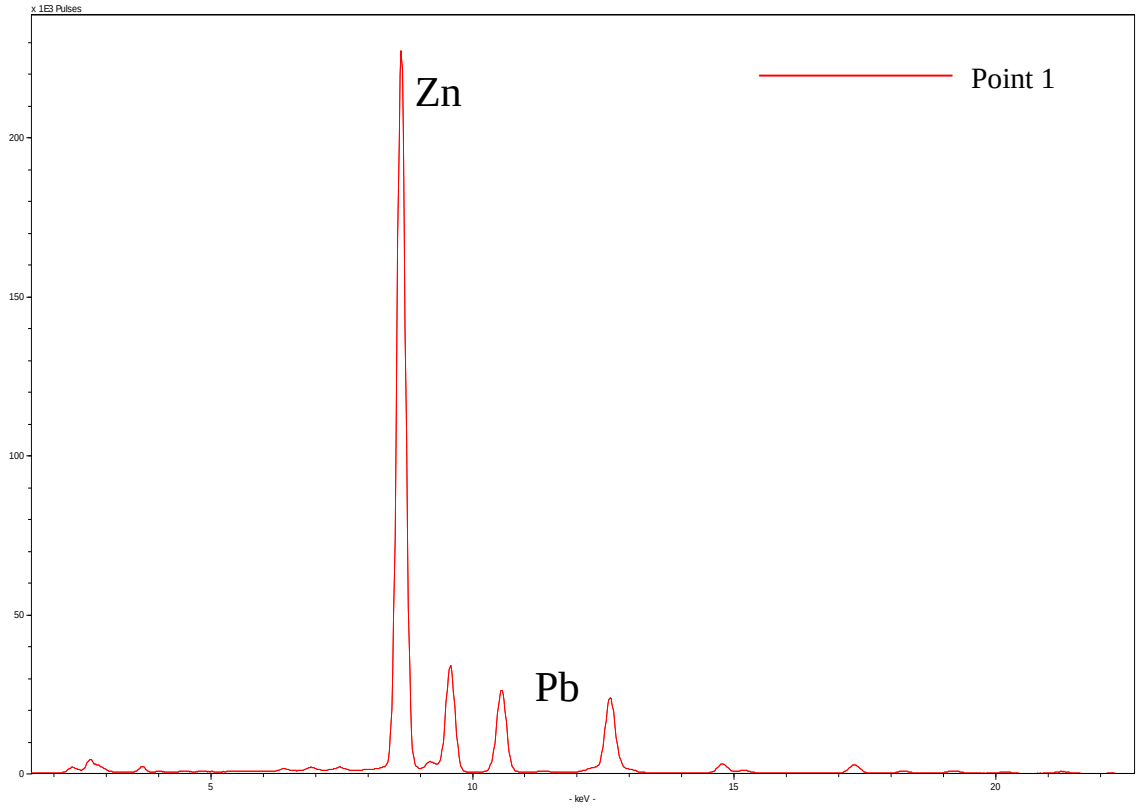

Figure 93. *Bluebonnets at Sunset San Antonio*. Point 1, white.

Green

Points 2 and 5 have peaks for zinc and lead like point 1, as well as peaks for cobalt, iron, chromium, barium, and cadmium, strontium and sulfur (figure 94). The cobalt, when comparing the spectra for these two points to those of 3 and 4, is coming from a cobalt-based blue. The chromium, strontium, and barium are indicators of lemon yellow, which is the common name for both barium yellow and strontium yellow ($BaCrO_4$ vs. $SrCrO_4$). The cadmium and sulfur are most likely cadmium yellow (CdS). Interestingly, the presence of yellow pigments indicates that the chromium is accounted for by lemon yellows, not chromium green. This points to a green made by blending blues and yellows and not a stand-alone green pigment as seen in past paintings.

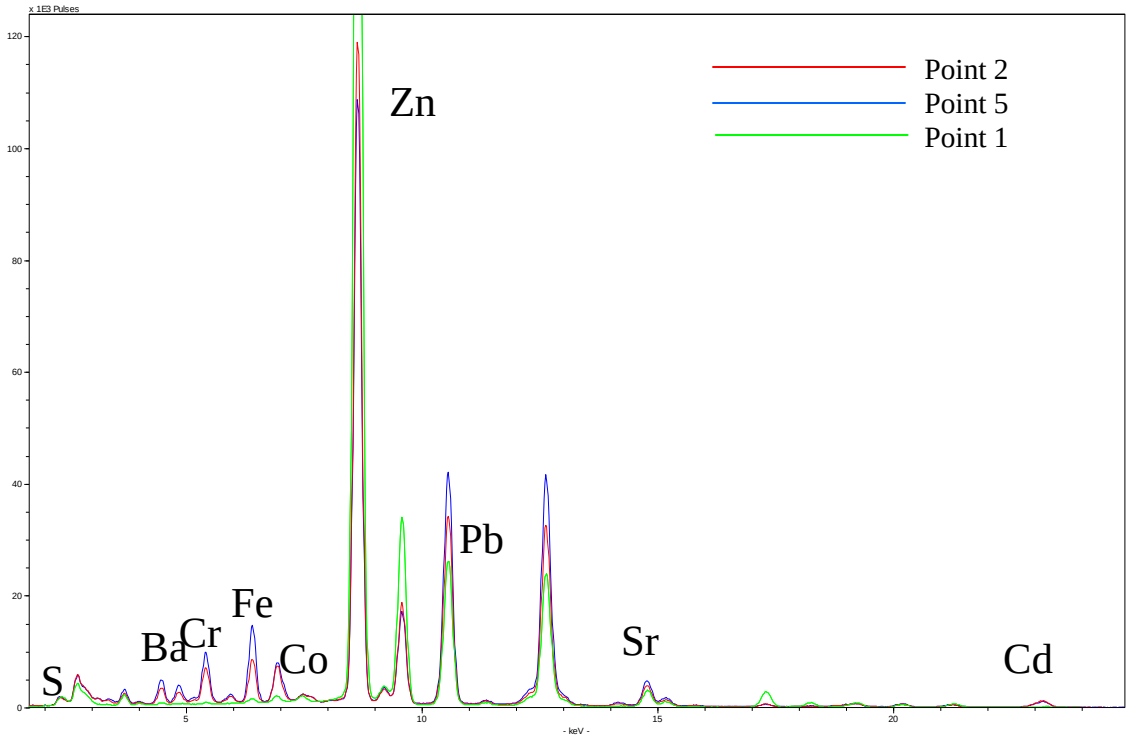

Figure 94. *Bluebonnets at Sunset San Antonio*. Points 2 and 5, greens, compared to point 1, white.

Blue

Points 3 and 4 are the blues, and like many of the cobalt-based blues in previous paintings, the presence of cobalt and tin indicates cerulean blue (figure 95). Point 3, the lighter shade of blue, has a smaller peak for cobalt and a higher peak for lead and zinc, indicating the mixing of the cerulean blue with zinc and lead whites.

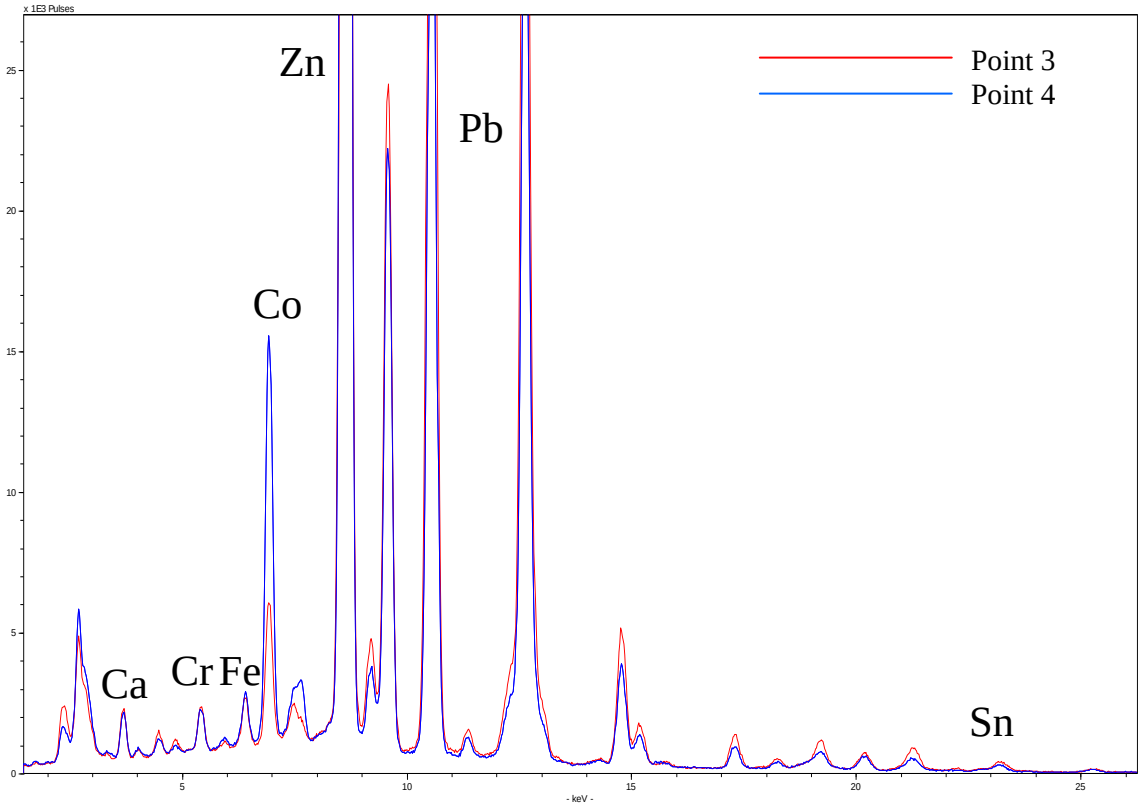

Figure 95. *Bluebonnets at Sunset San Antonio*. Points 3 and 4, blues.

Signature

The signature of point 6 has distinct chromium, barium, strontium, and cadmium peaks when compared to the blues of points 3 and 4 (figure 96). As mentioned above, the chromium and barium are likely present as barium yellow. Comparing point 6 to the green of point 5, the peaks for cobalt and iron are smaller, and compared to point 4, the blue, the peaks for barium, strontium and chromium are higher. This seems to indicate a higher concentration of yellow mixed with the blue, which would lead to a darker, browner looking green color that matches the hue of the signature.

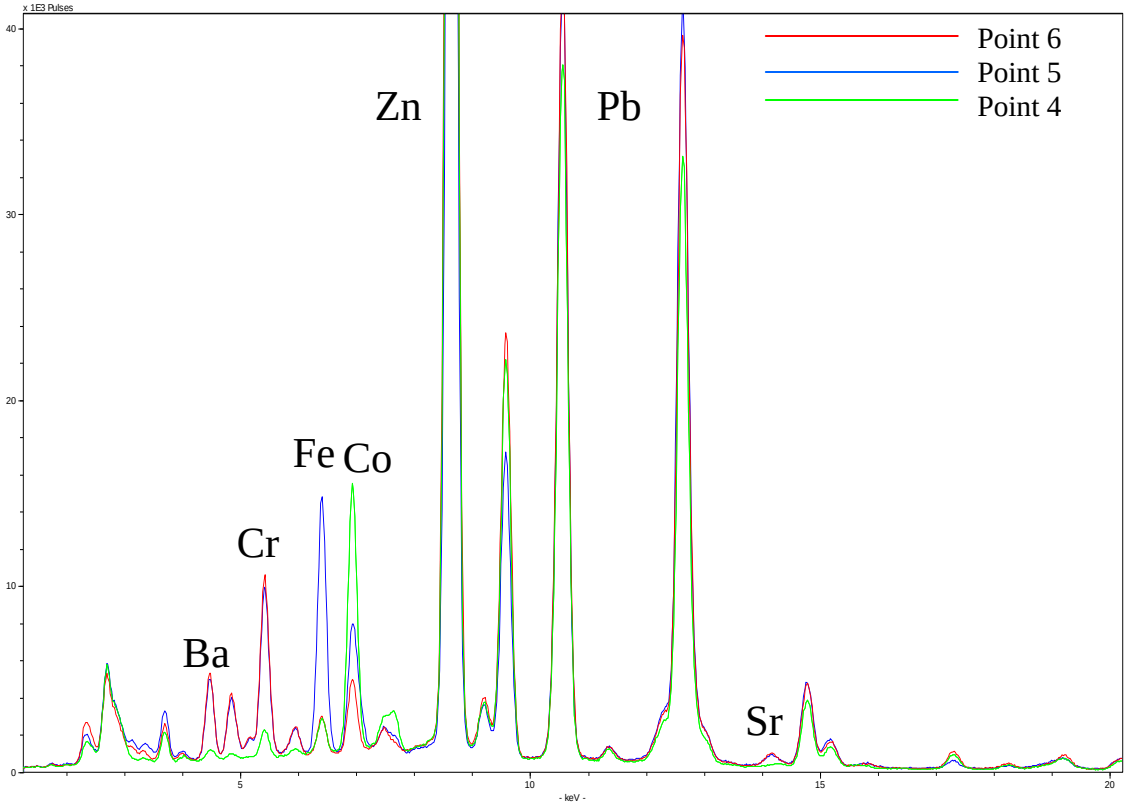

Figure 96. *Bluebonnets at Sunset San Antonio*. Point 6, the signature, compared to point 5, the green and point 4, the blue.

A White Road at Late Afternoon

Figure 97. *A White Road at Late Afternoon*. 1921, Signed Julian Onderdonk, Oil on Canvas, 7in x 10in, Witte Museum, San Antonio, TX.

For *A White Road at Late Afternoon* (figure 97), ten points were analyzed. Initial planning had mapped eleven points, but the distance between points 6 and 8 and the planned point 7 were too close to be effectively insulated from one another, so point 7 was omitted. Point 1 is the white of the cloud, point 2 is the yellow of the road, points 3, 5, 6, and 8 are the various hues of blue, point 4 is the pinkish orange of the bush, point 9 is the dark green of leaves, point 10 is a salmon color on the right of the painting, and point 11 is the signature.

White

All points in *A White Road at Late Afternoon* have a high zinc peak, indicating that this painting was primed and painted with a zinc white. The white of the cloud has a yellow tinge to it, and given the strong barium and strontium peaks, this initially seems like a good candidate for strontium and barium yellow, or lemon yellow (figure 98). However, neither the white nor the yellow points have any evidence of chromium present, necessary for the formulation of either variety. The barium peak is highest in the white point, perhaps indicating barium white ($BaSO_4$).

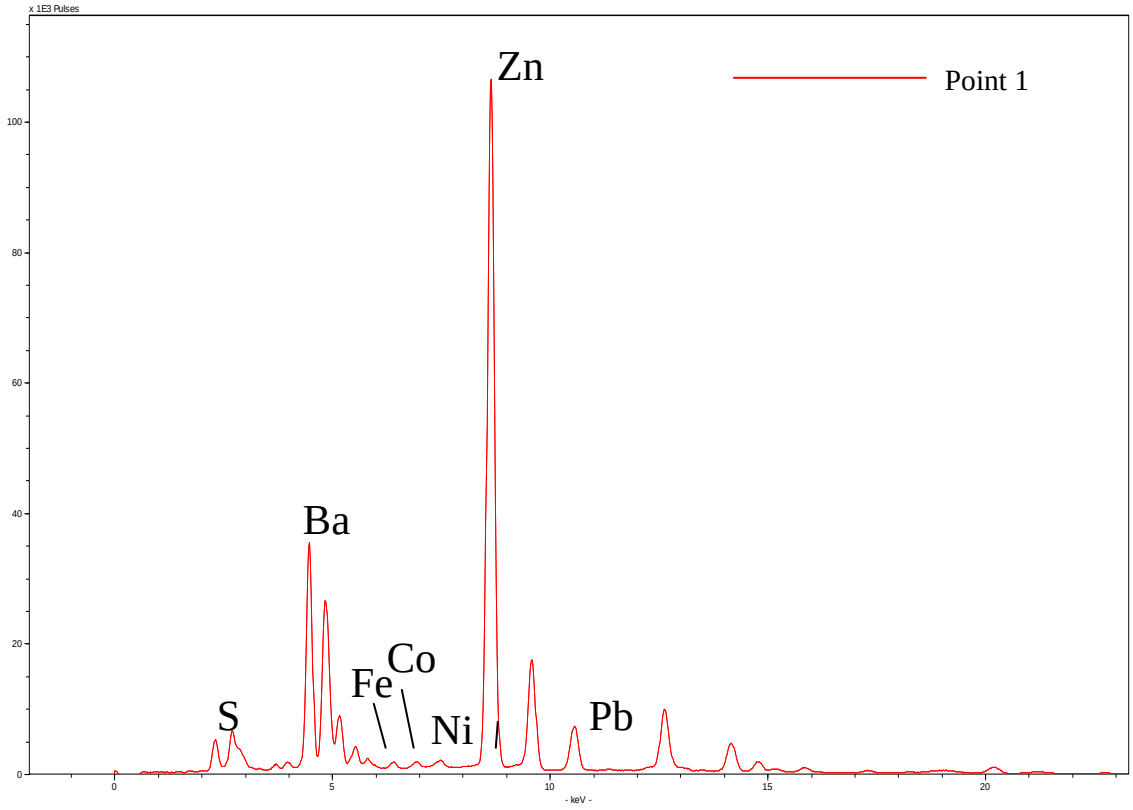

Figure 98. *A White Road at Late Afternoon*. Point 1, white.

Yellow

The yellow of the road appears to have been painted atop the white, and the spectrum for point 2 reflects this. Point 2 is very similar in composition to point 1, with higher peaks from iron, lead, zinc and cobalt (figure 99). Both lead and zinc can be constituent parts of yellow pigment, but without the presence of antimony, tin, or chromium, neither is likely to contribute to the yellow hue. Instead, it is most likely that the yellow is an iron-based limonite.

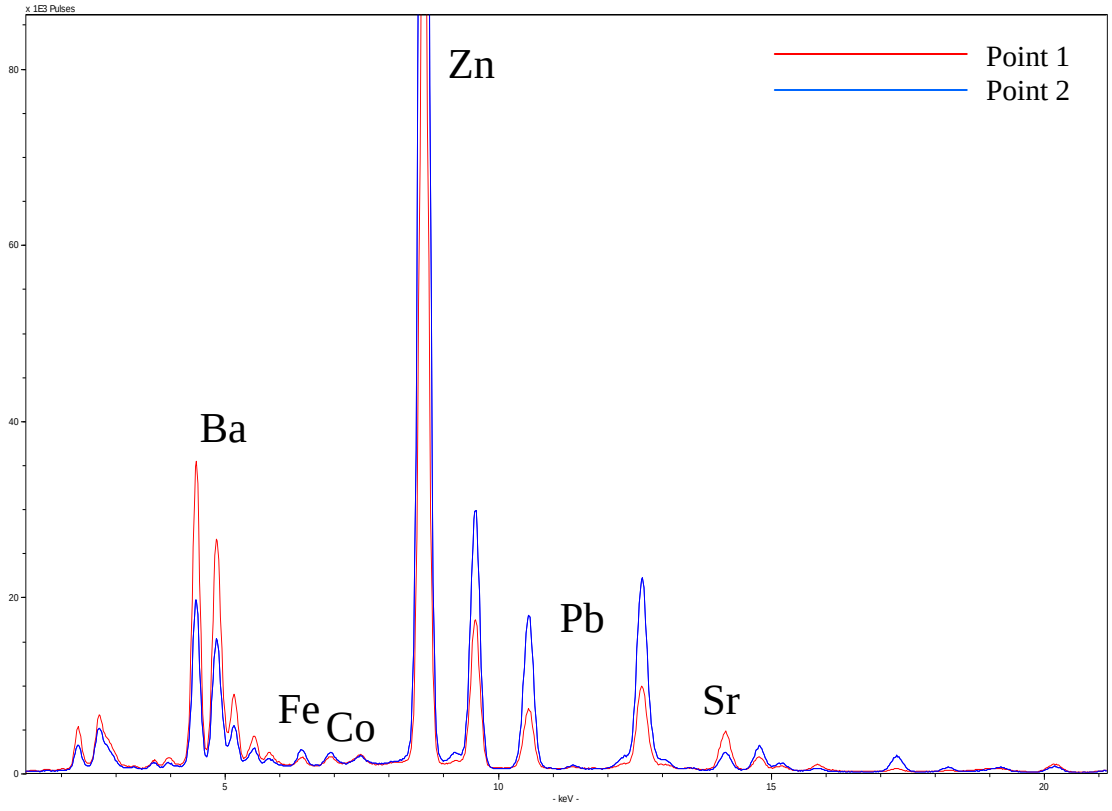

Figure 99. *A White Road at Late Afternoon.* Point 1, white, compared to point 2, yellow.

Blue

Comparing the various hues of blue in points 3, 5, 6, and 8, the common trend is that the darker the blue, the higher the cobalt peak (figure 100). As with several of the previous paintings, the blues contain cobalt but not the additional elements expected for traditional cobalt blues. This suggests that the pigment being used was smalt, a ground up cobalt colored glass (Artioli 2010, 269).

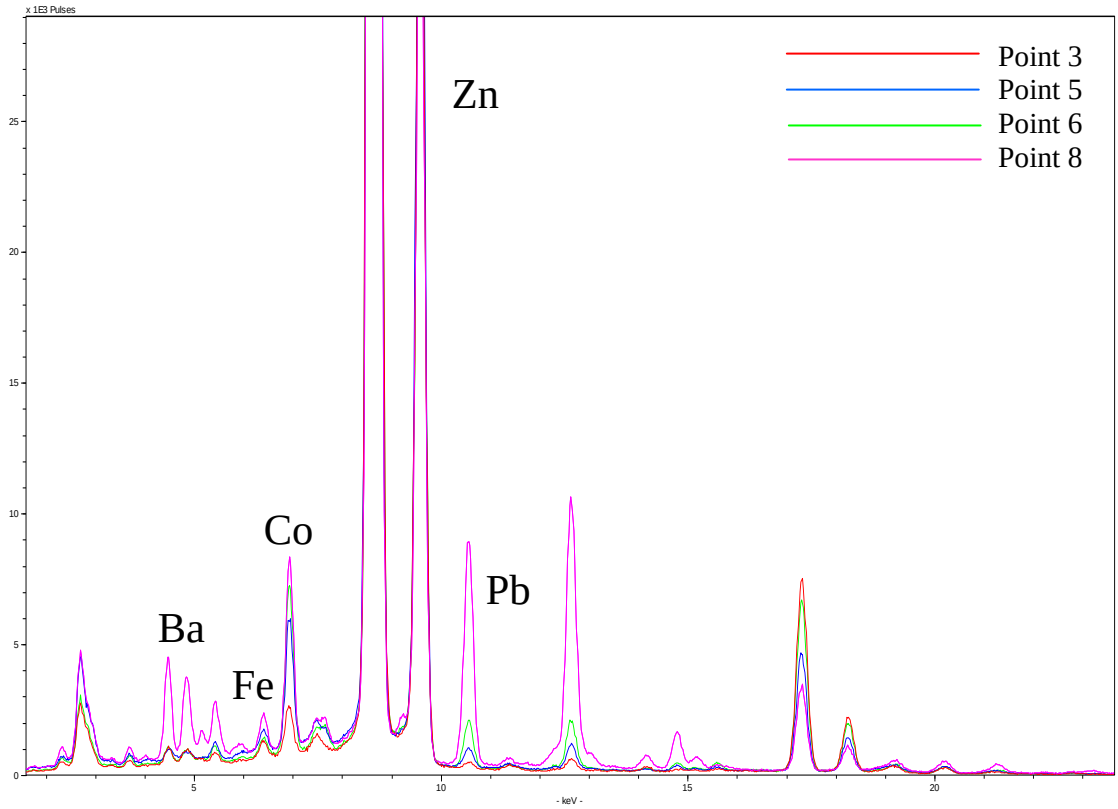

Figure 100. *A White Road at Late Afternoon*. Points 3, 5, 6, and 8, various hues of blue.

Pink and Orange

The pink and orange or point 4, as well as the salmon color of point 10, both proxies for red, both have a distinct iron peak (figure 101). This suggests the use of an iron based red like hematite or ochre.

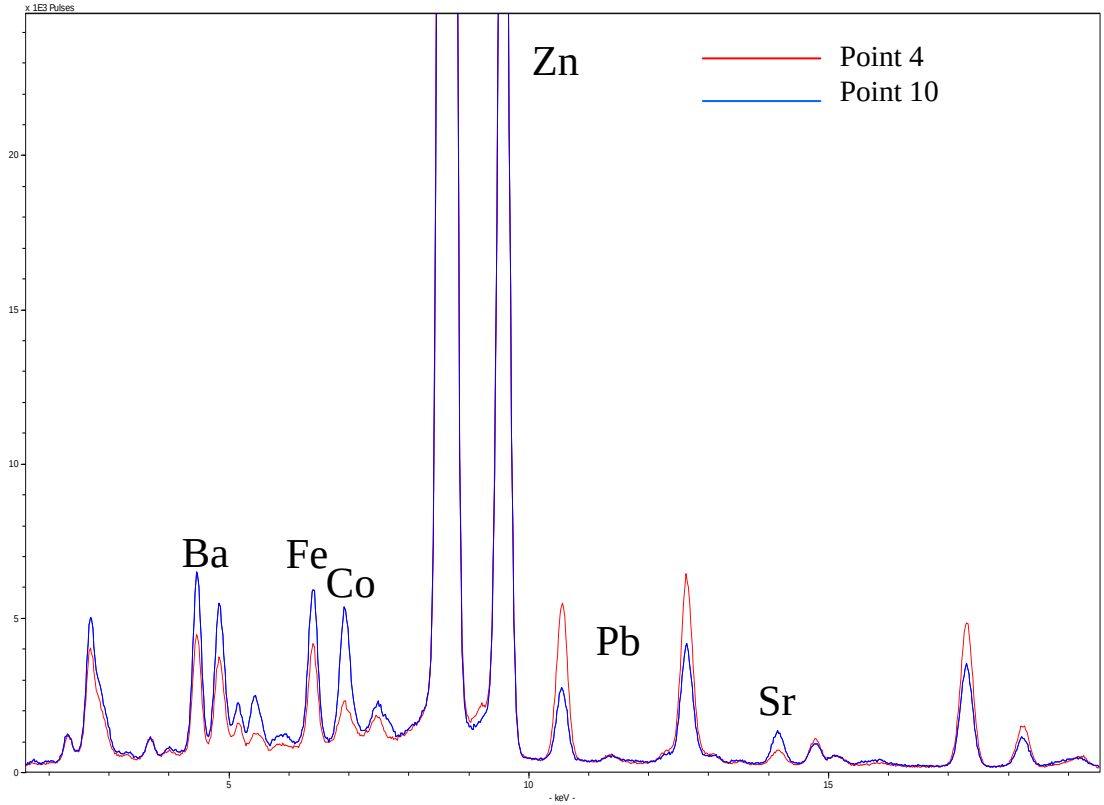

Figure 101. *A White Road at Late Afternoon*. Point 4, pink and orange, and point 10, salmon.

Green and Signature

The green of point 9 is the only point other than the signature in the painting that contains chromium, indicating that it is chromium oxide, or emerald green (Cr2O3). The signature, point 11, contains chromium as well, but it is likely from the smattering of green behind it (figure 102). The most pronounced peaks of interest in the signature are the iron and the cobalt peaks, indicating that the dark color of the signature is a blend of red and blue.

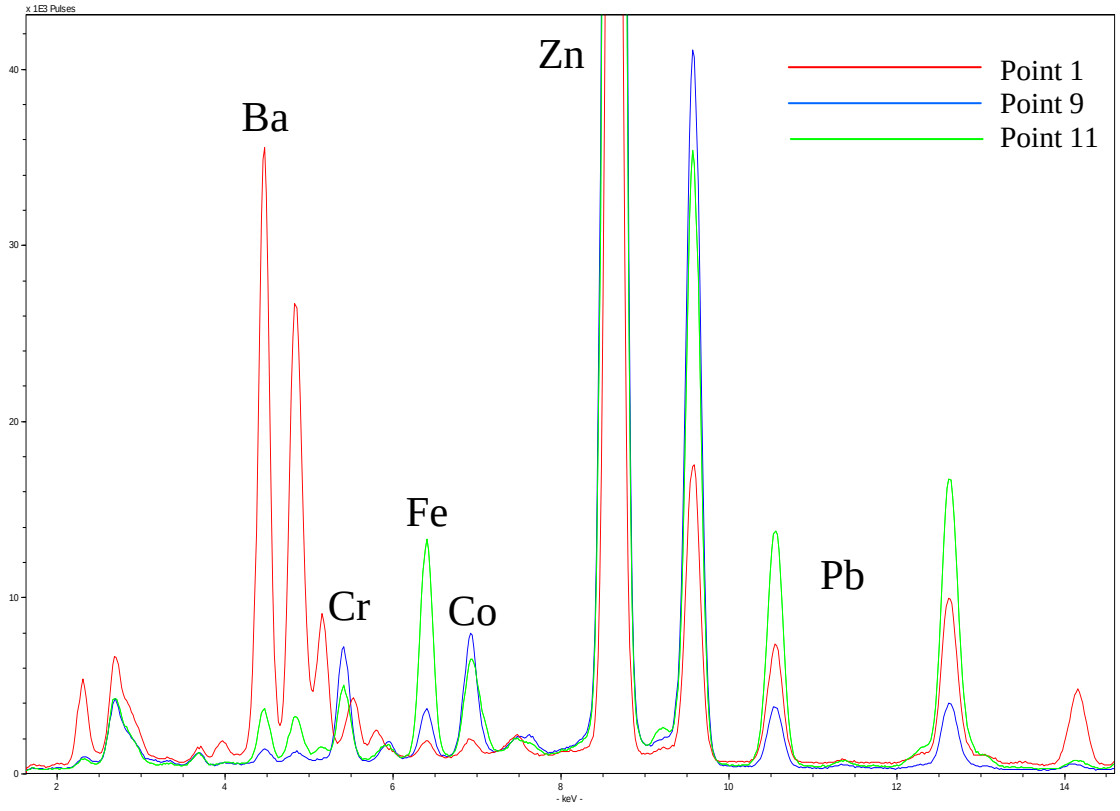

Figure 102. *A White Road at Late Afternoon*. Point 1, white, compared to point 9, green, and point 11, the signature.

Miles and Miles of Bluebonnets

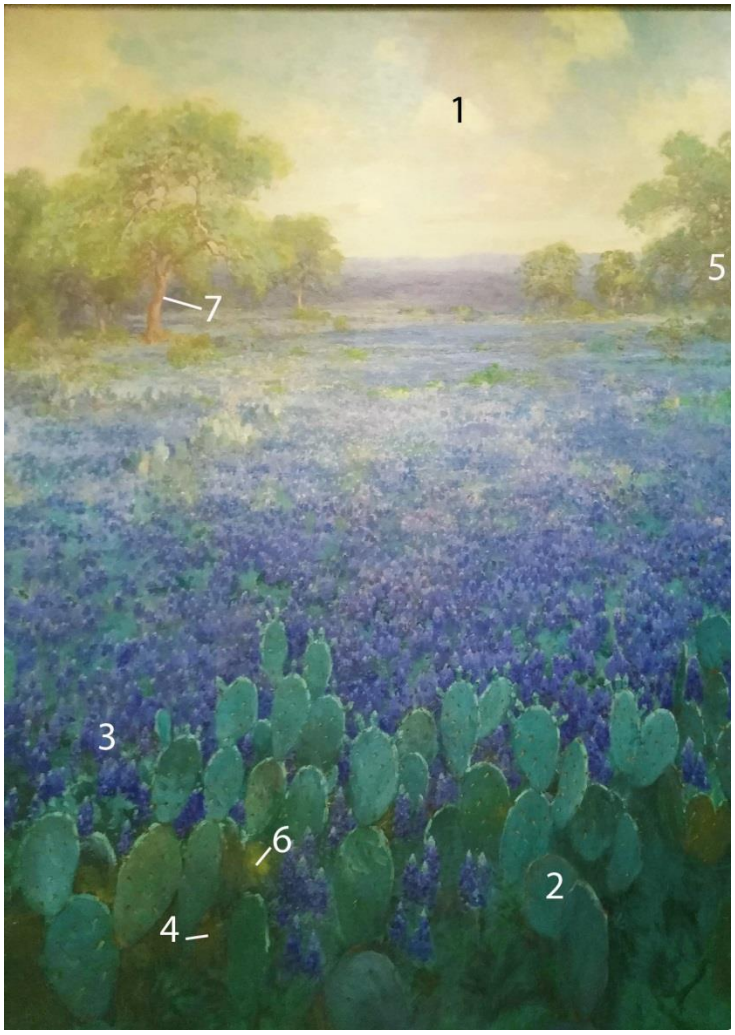

Figure 103. *Miles and Miles of Bluebonnets*, 1921, Signed Julian Onderdonk, Oil on Canvas, Stark Galleries, Texas A&M University.

For *Miles and Miles of Bluebonnets* (figure 91), seven total points were taken. Point 1 is the purest white of the sky, point 2 is the green of the cacti, point 3 is the blue of the bluebonnets, point 4 is the ochre between the cacti leaves, points 5 and 7 are the

browns of the trees, and point 6 is the yellow highlight on the back of a cacti. Although lead is the primer and would appear to be the primary white paint, the highlight of the cloud contains titanium. The occurrence of titanium white in any of Onderdonk's paintings requires investigation; even though small experimental batches of the titanium white paint were being formulated as far back as 1916, the availability of titanium white was limited to European artists working with chemists researching pigments. In 1919, titanium white was manufactured by a Norwegian company for commercial use, but it was not until the mid-1920s that it was being supplied to artists. Even then, real acceptance by the art community did not occur until the 1930s (Eastaugh et al. 2008, 370). This painting is dated 1921, and the likelihood that Julian Onderdonk had titanium white in his palette is very low. The appearance of titanium white at this stage in Onderdonk's career can mean one of three things: First, and least likely, he could have had access to titanium white. Second, and still very unlikely, this painting is a copy or a fake. Third, and the most likely explanation, is that this painting has been restored by someone who either did not know or did not care that Onderdonk did not have access to titanium white.

White

As mentioned, the white of point 1 has a strong peak for titanium. The only other point in the painting with a trace of titanium is number 2, the green of the cacti (figure 104). Either the original green was blended with titanium white to lighten it, or a white highlight was restored with titanium white at a later date. Either way, given the peaks in the rest of the spectra, zinc appears with the most intensity in every point but point 1, and therefore it is likely that the painting was primed with a zinc white.

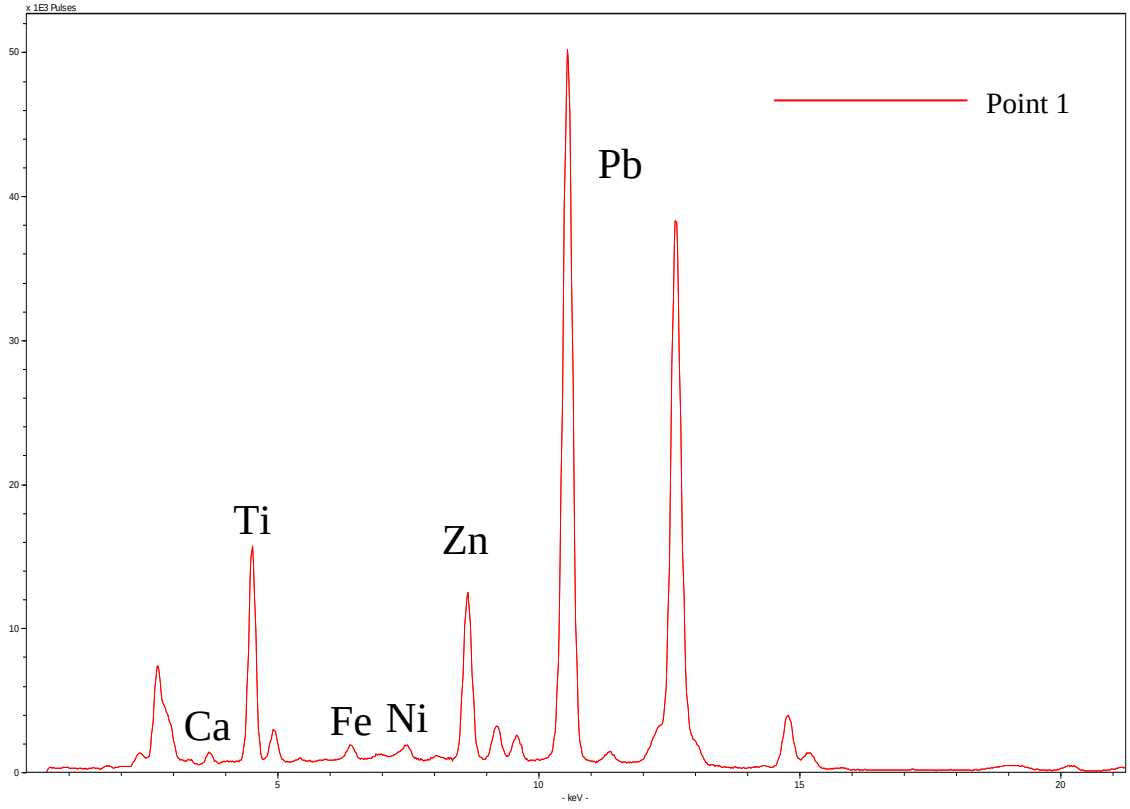

Figure 104. *Miles and Miles of Bluebonnets*. Point 1, white.

Green and Yellow

The green of point 2 is characterized by its chromium peak, indicating chromium oxide, or emerald green (figure 105). The chromium could also indicate the use of strontium yellow, which could be mixed with cobalt blue to achieve a green color, but the cobalt peak is higher in point 6, the yellow. If the green were a mix of strontium yellow and cobalt blue, there would be more cobalt in the green than the yellow. The presence of chromium does mean that it is possible that the yellow is a zinc yellow ($ZnCrO_4$), though the zinc peaks between the two are nearly identical, while the green peak actually has a higher energy peak for strontium. It is likely that the yellow is in fact strontium yellow, and was mixed with the chromium oxide green to lighten the color.

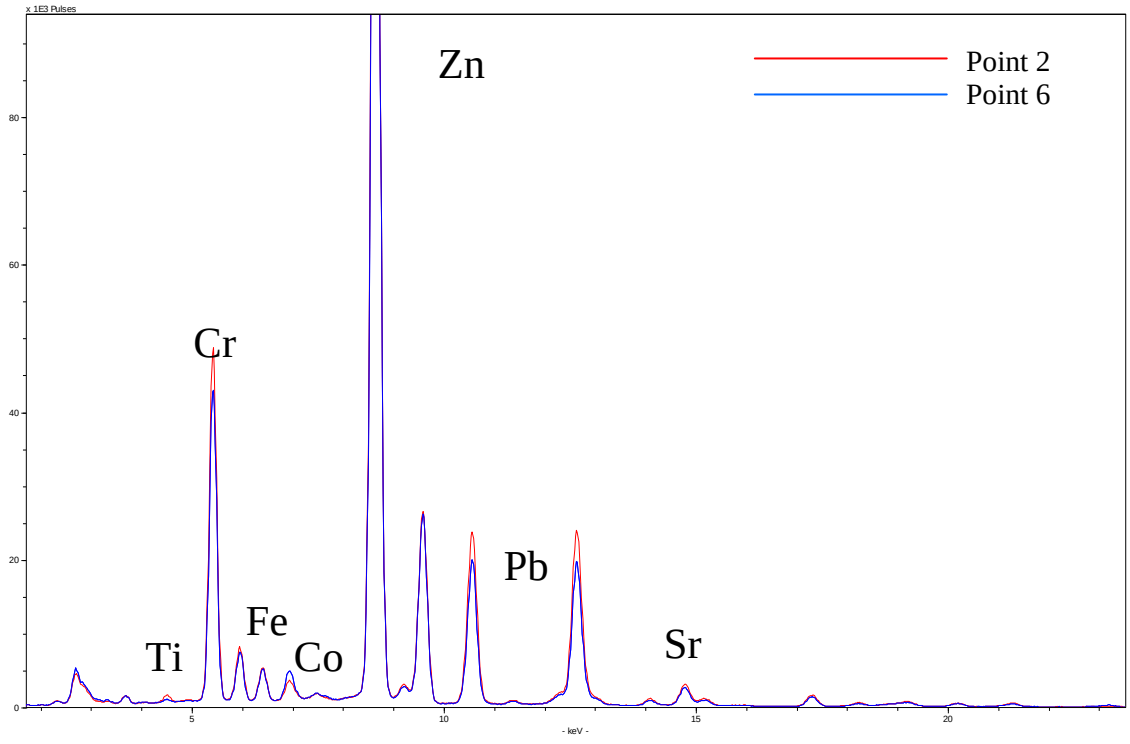

Figure 105. *Miles and Miles of Bluebonnets*. Point 2, green, compared to point 6, yellow.

Blue

Apart from the zinc peak, the highest peak for the blue of point 3 is cobalt (figure 106). There is also a minute amount of tin, indicating that this is possibly a cerulean blue, though given the trace amount it is just as likely another variant of a cobalt based blue like smalt.

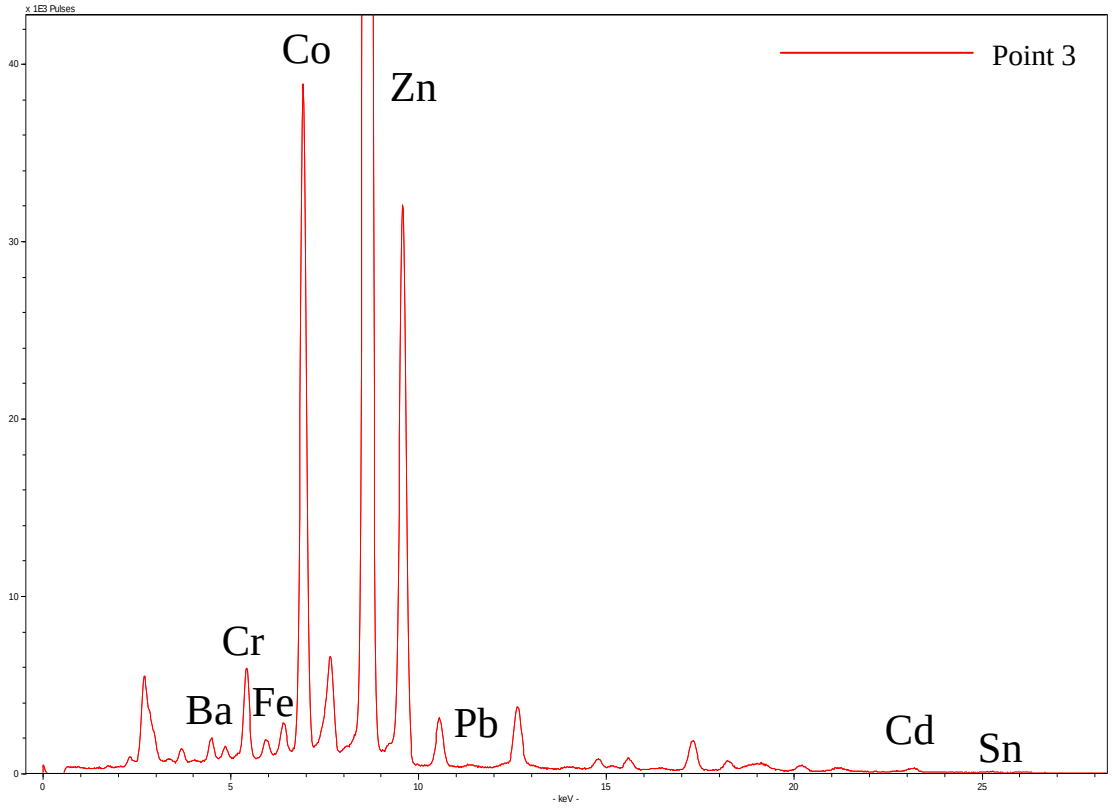

Figure 106. *Miles and Miles of Bluebonnets*. Point 3, blue.

Ochre and Brown

The ochre color in point 4 is iron based, as was expected. The browns of points 5 and 7 also have good peaks for iron, and interestingly, both have lead peaks that the ochre does not (figure 107). The ochre is also higher in cobalt, which indicates that the yellow was painted directly atop the blue of the flowers instead of the chromium green of the cacti. The brown of point 5 has a higher peak for chromium than the other two, and given its proximity to the green leaves around it, this is not surprising.

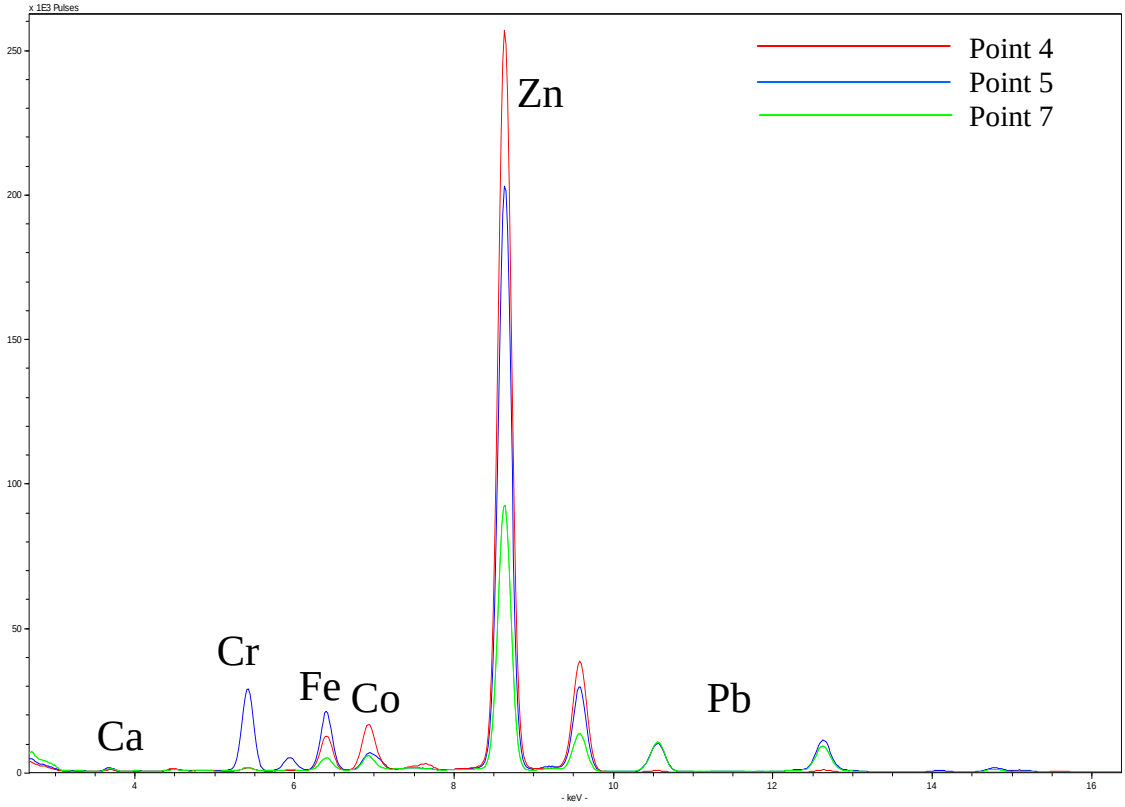

Figure 107. *Miles and Miles of Bluebonnets*. Point 4, ochre, and points 5 and 7, browns.

Dawn in the Hills

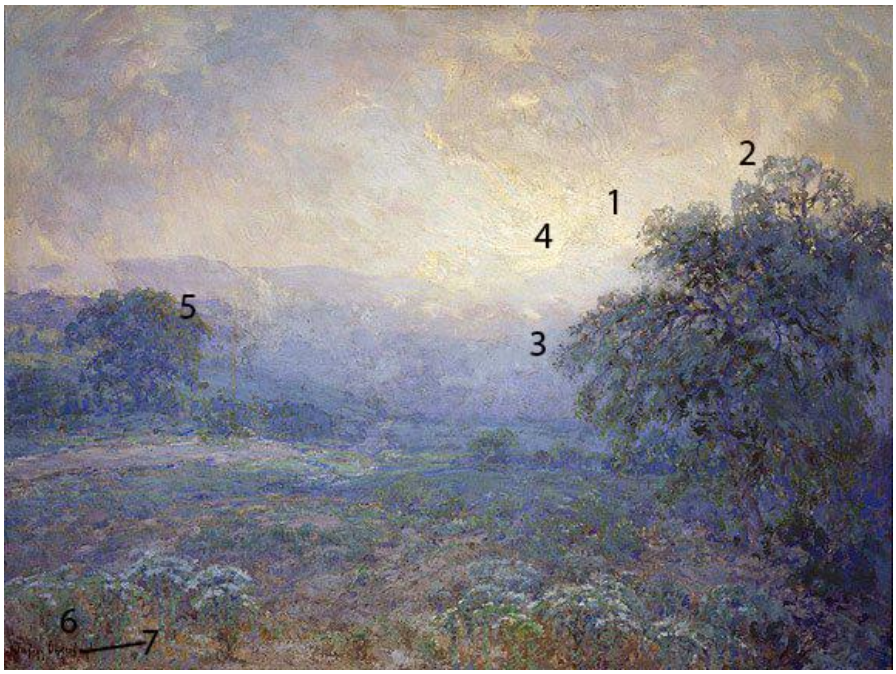

Figure 108. *Dawn in the Hills*. 1922, Signed Julian Onderdonk, Oil on Canvas, 30in x 40in, Witte Museum, San Antonio, TX.

Dawn in the Hills (figure 108), apart from being a particularly beautiful painting in its own right, is highly treasured due to the fact that it is the last painting that Julian ever painted (Rudolph 2008, 40). The lack of titanium white here gives greater insight as to its presence in *Miles and Miles of Bluebonnets*. It is unlikely that if Onderdonk were indeed one of the first painters in the world to have access to the paint, that he would discontinue using it so soon. A total of seven points were analyzed for this painting. Points 1 and 2 are the whites of the sky, points 3 and 4 are blues, point 5 is the green of the tree to the left of the painting, point 6 is the reddish background in the lower left-hand corner, and point 7 is the signature.

White

The white of the clouds in points 1 and 2 appears to be a zinc white and a lead white (figure 109). Both zinc and lead peaks are consistent across all peaks, and so it stands to reason that the painting was primed with both.

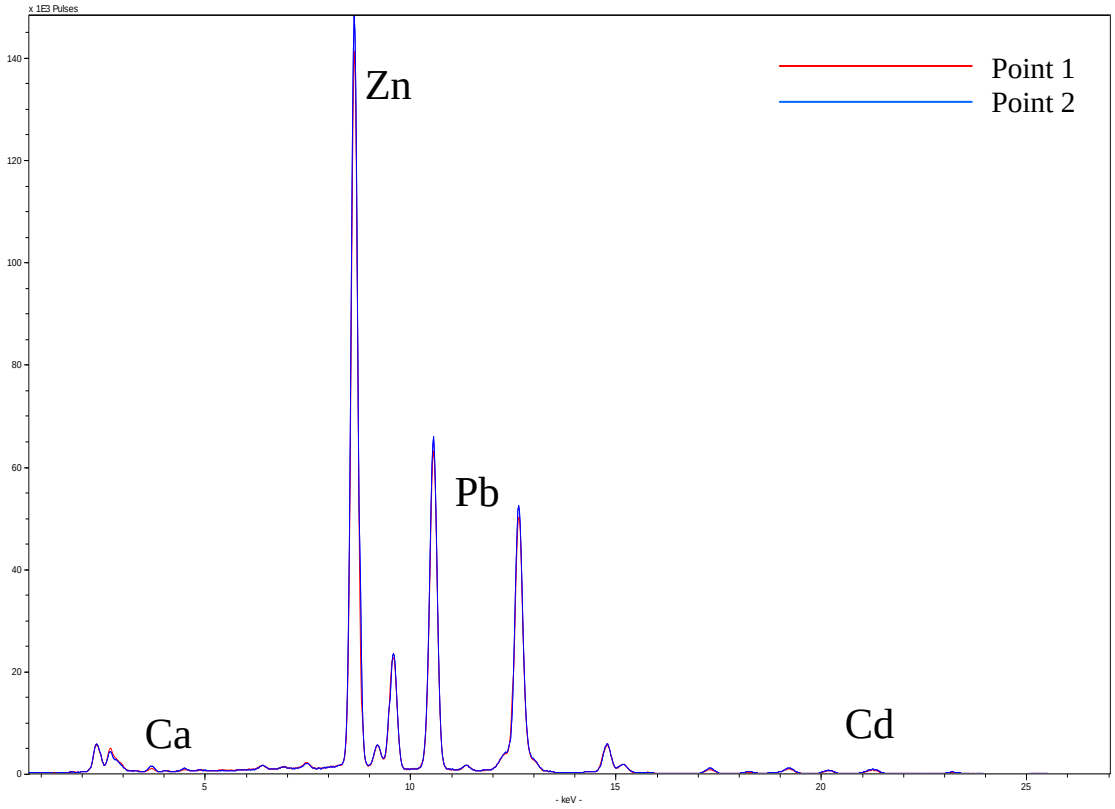

Figure 109. *Dawn in the Hills*. Point 1 and 2, white.

Blue

Both blues of points 3 and 4 are clearly cobalt based when compared to the white spectrum of point 1 (figure 110). As with the rest of Onderdonk's paintings in the 1920s, this cobalt based blue does not have the indicative tin or aluminum peaks that would point toward cerulean blue or cobalt blue. Nonetheless, this cobalt signature is consistent with the other blues in Onderdonk's late period work.

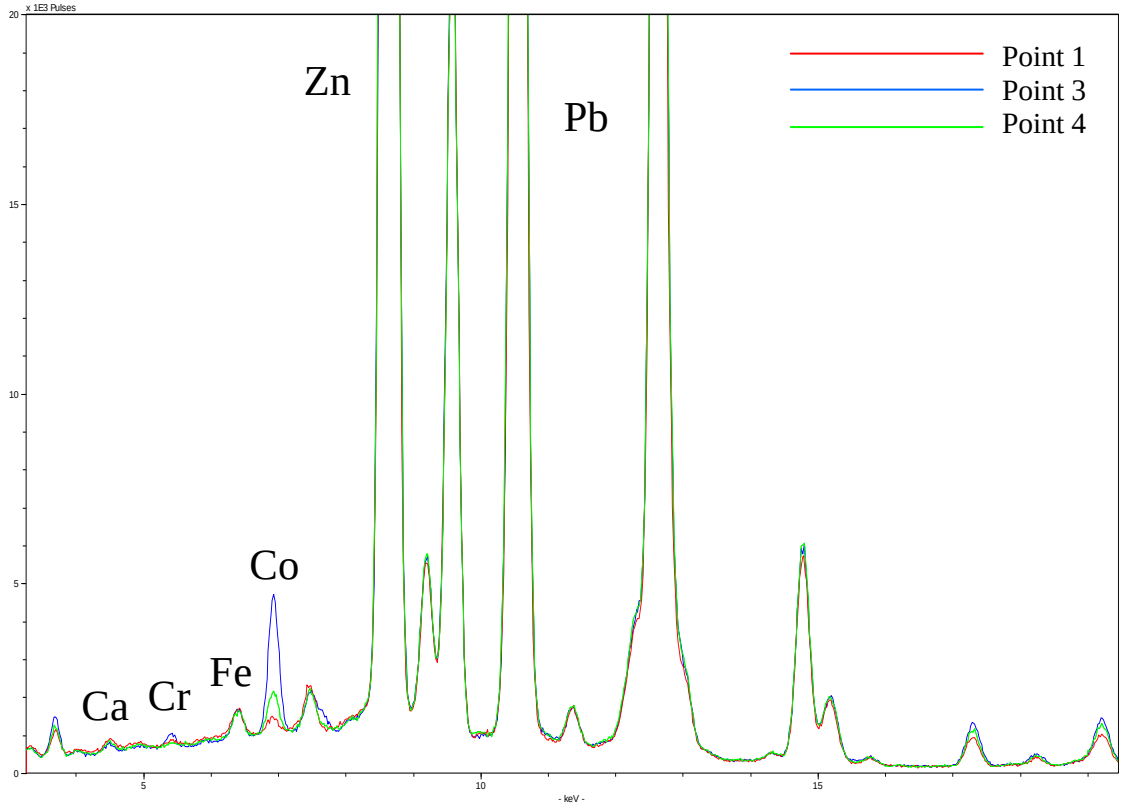

Figure 110. *Dawn in the Hills*. Point 1, white, compared to points 3 and 4, blues.

Green

As seen in figure 111 below, the green of point 5 is a chromium based green, almost certainly chromium oxide (emerald green).

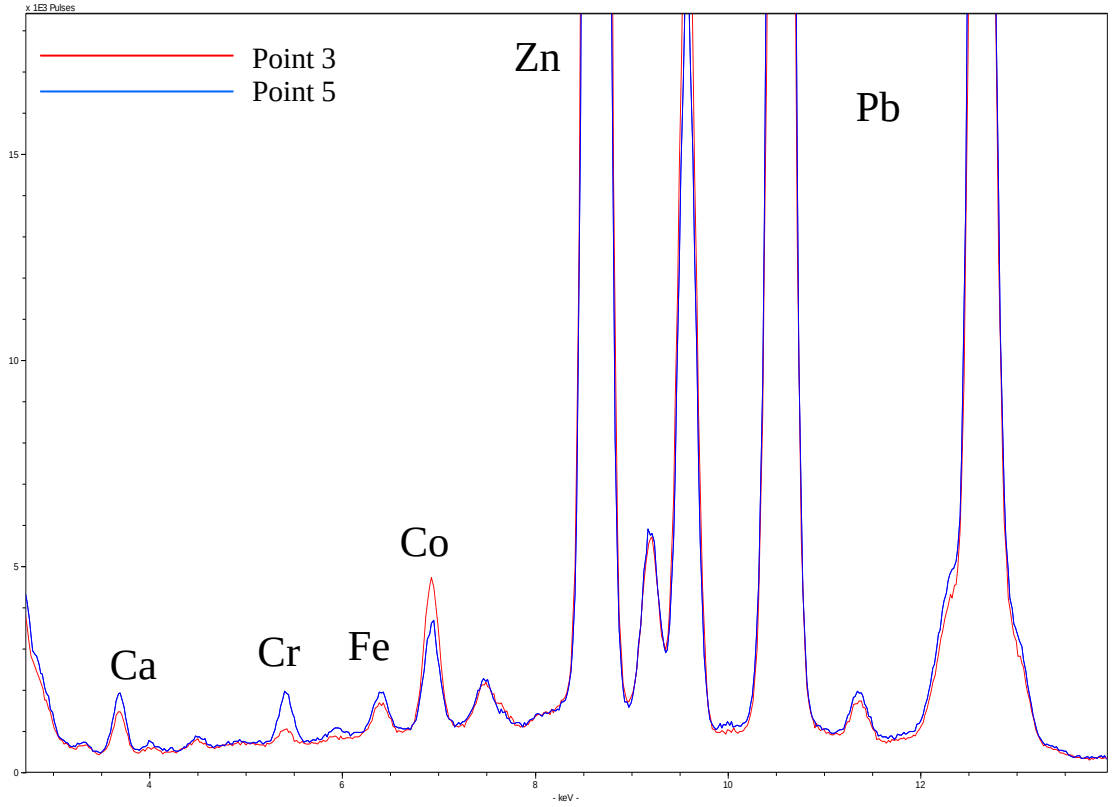

Figure 111. *Dawn in the Hills*. Point 5, green, compared to point 3, blue.

Red and Signature

The area behind the signature is a reddish orange, which appears to be iron based, indicating hematite. In point 6, there is also a trace of mercury, indicating that the red highlights are vermillion (HgS) instead of iron. Point 7, the signature, has a slightly higher peak for chromium, likely indicating that the red and green were mixed to make a darker color (figure 112).

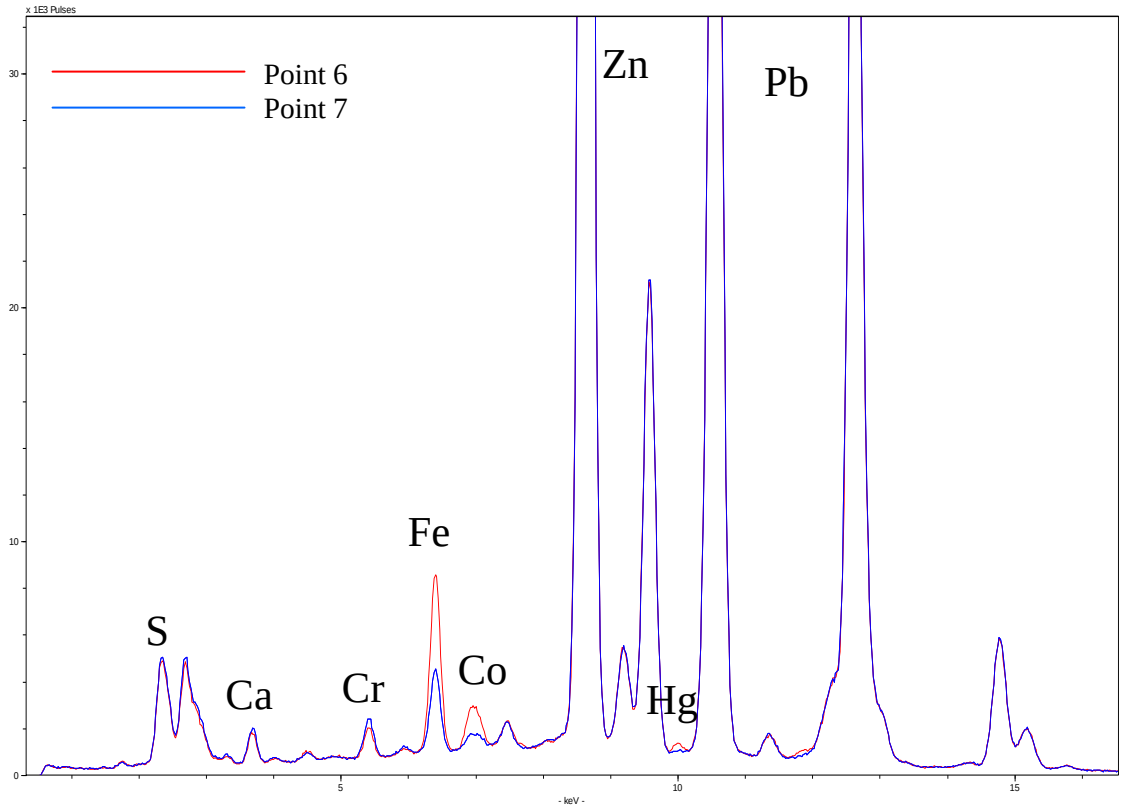

Figure 112. *Dawn in the Hills*. Point 6, red, compared to point 7, the signature.

Pastoral with Lady in Red

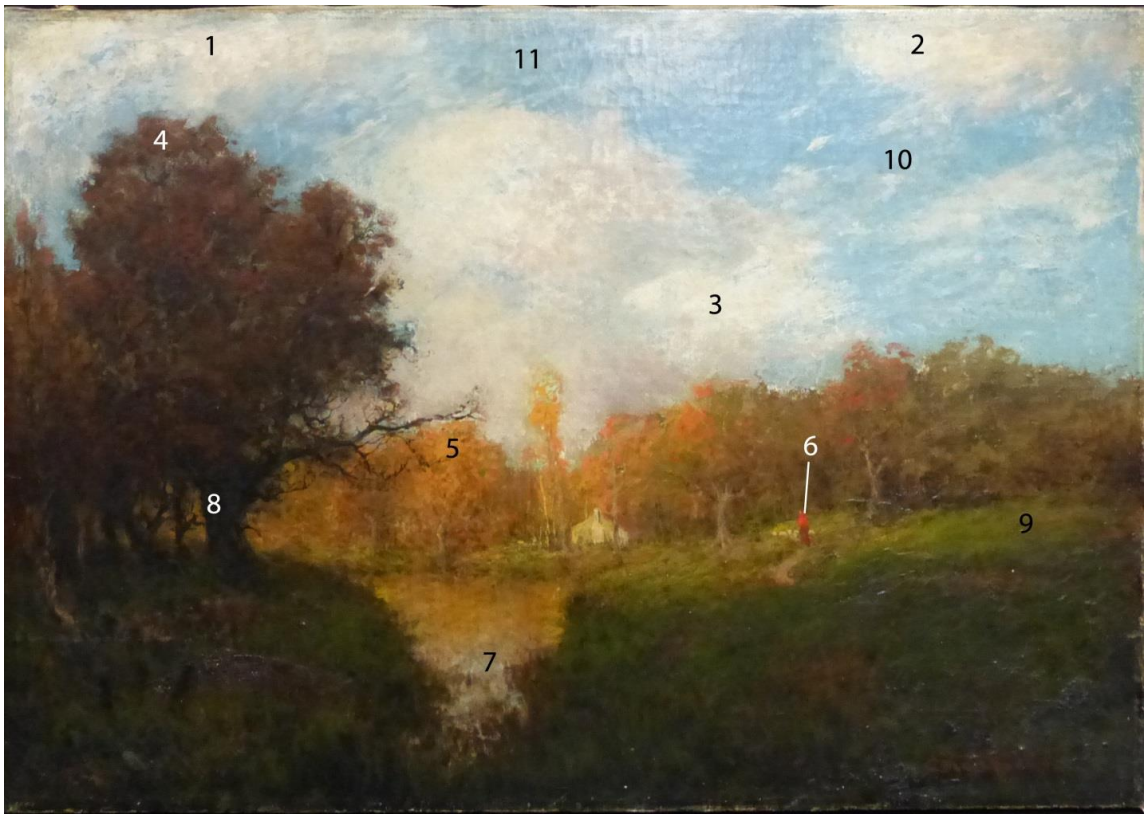

Figure 113. *Pastoral with Lady in Red*. No Date, Signed Chase Turner, Oil on Canvas, 14in x 20in, James and Kimel Baker Collection, College Station, TX.

For *Pastoral with Lady in Red* (figure 113), eleven points were analyzed. Points 1, 2, and 3 are whites from the sky, points 4, 5, and 6 are hues of red and orange, 7, 10, and 11 are blues, 8 is brown, and 9 is green.

White

The whites, points 1-3, are lead based, with some zinc, barium, iron, and nickel (figure 114). This is a lead white, consistent with Onderdonk's earlier works. The zinc could represent either zinc white, or, more likely, it represents the zinc yellow, as seen in the analysis of the reds. The barium peak might indicate the use of *Blanc fixe*, a barium sulfate white introduced around 1830 that is known to be a particularly brilliant white (Wehlte 1967, 69)

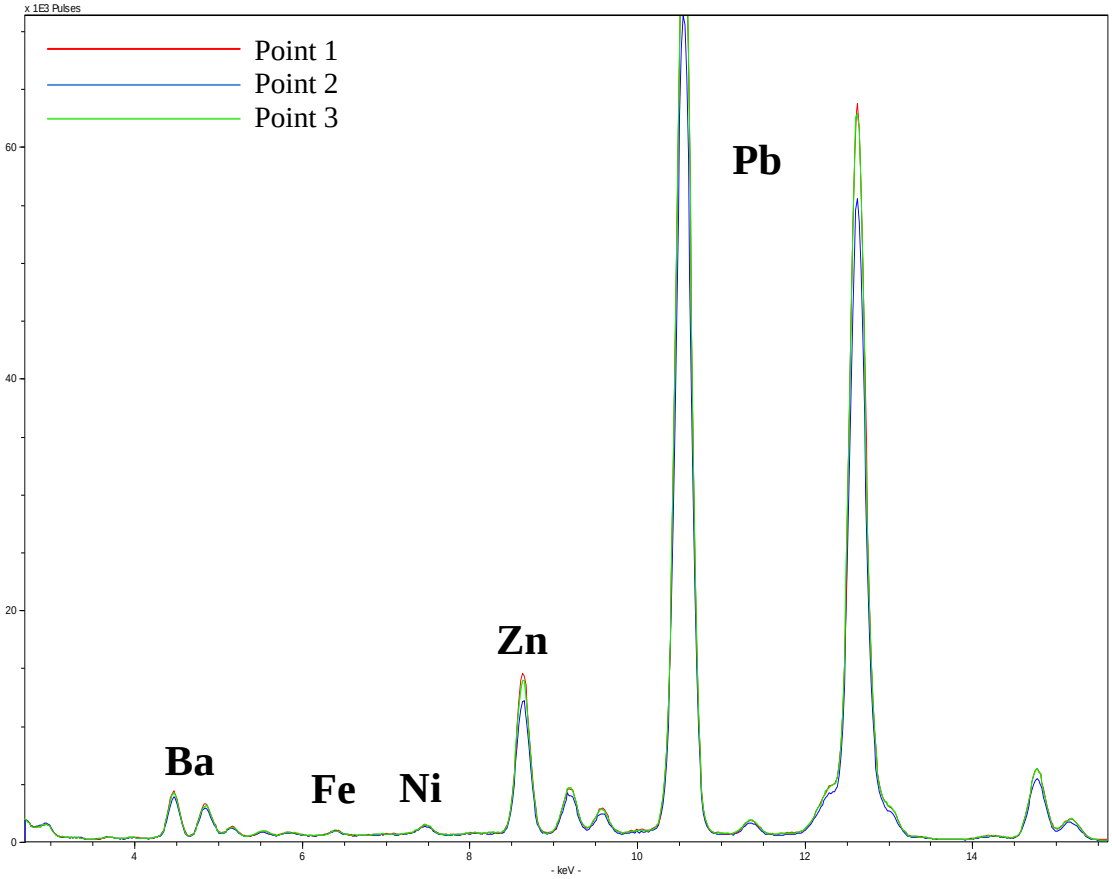

Figure 114. *Pastoral with Lady in Red*. Points 1, 2, and 3, whites.

Red

Point 4 is a reddish brown from the tree on the left, point 5 is a lighter orange from the tree in the background center left, and point 6 is the bright red of the figure to the right. All three reds are clearly mercury based (figure 115). Of the three, point 4 has the strongest iron signal, point 5 has the strongest zinc signal, and point 6 has the strongest chromium signal. Based on this, point 4, the dark red, has a blend of the mercury red and a darker iron based pigment, similar in energy to the iron of the brown and the green. For point 5, the higher zinc level points to zinc yellow mixed with the mercury. Point 6, the truest red, is painted very delicately atop the green grass, and the chromium there is likely from the viridian green.

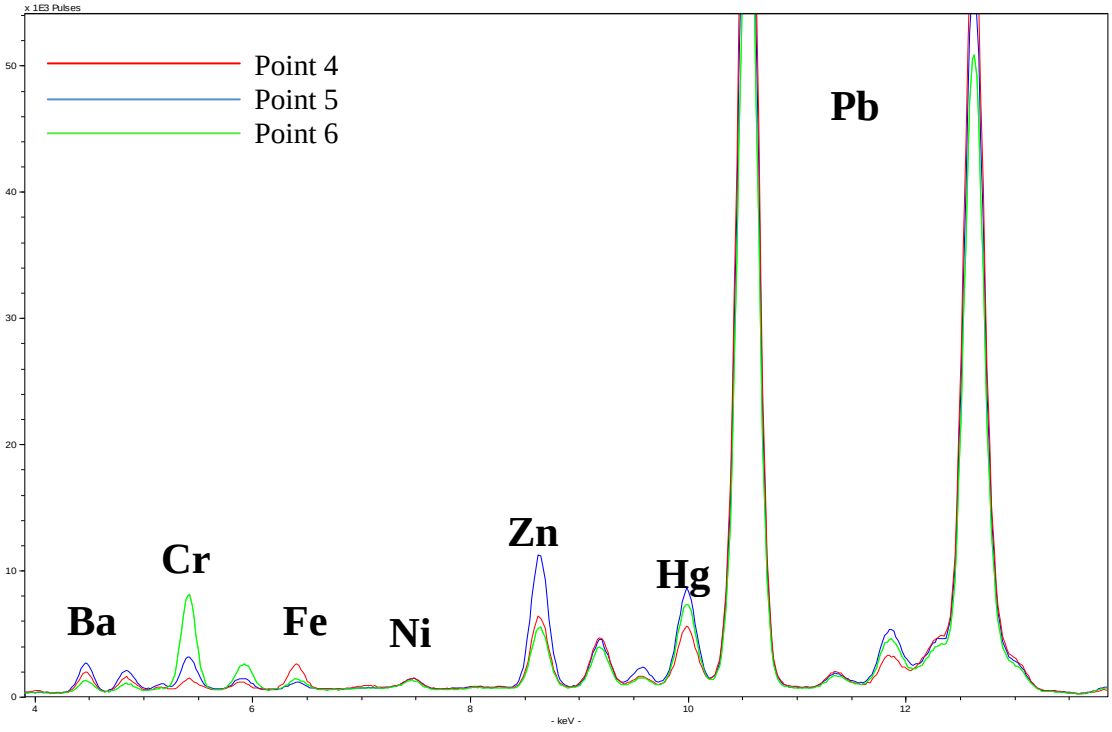

Figure 115. *Pastoral with Lady in Red*. Points 4, 5, and 6, reds.

Blue

Points 7, the blue of the water, and 10 and 11, the blues of the sky, all bear a very strong resemblance to the white pigments (figure 116). There are slightly elevated iron levels compared to the white, so it is possibly an iron based blue, like Prussian blue, though it is also possible that the blue is an organic based pigment like indigo that the XRF is not sensitive enough to identify. Point 7 shows higher mercury and less barium, but these are the result of the brown colors surrounding the water.

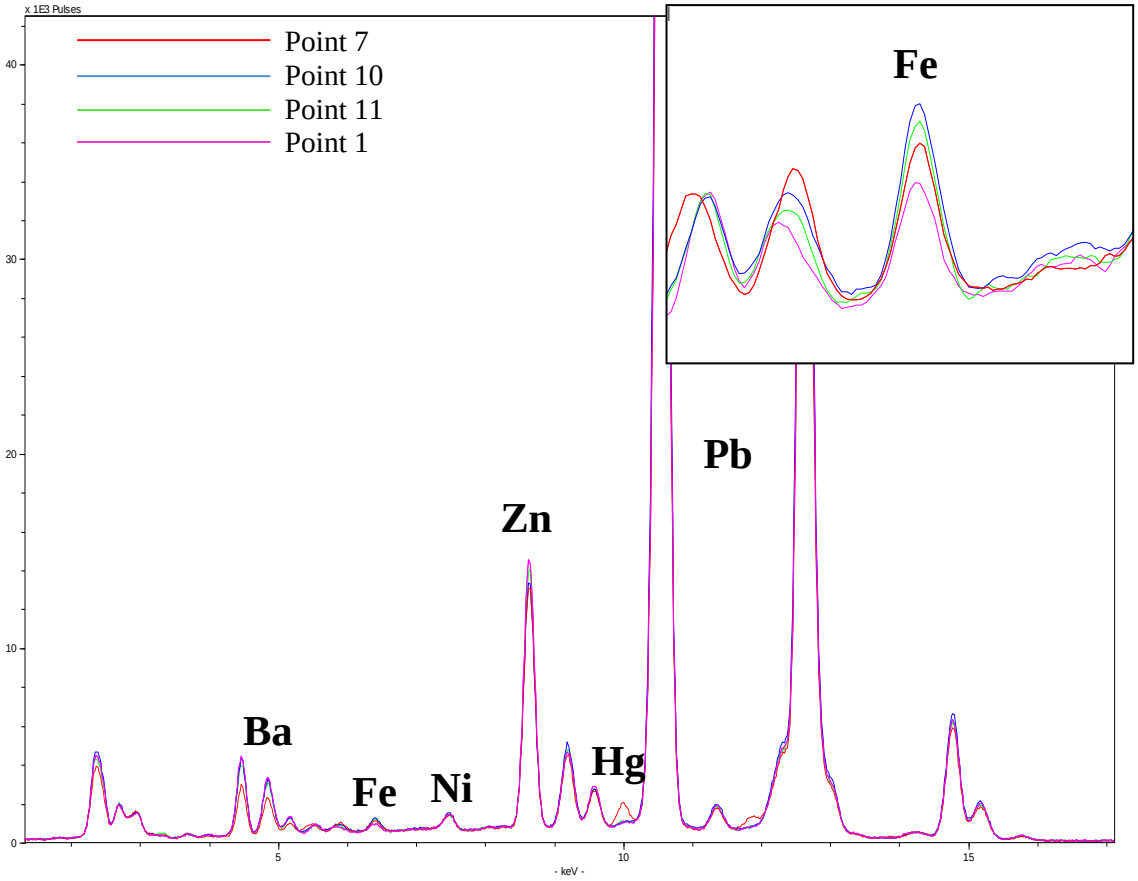

Figure 116. *Pastoral with Lady in Red*. Points 7, 10, and 11, blues, compared to point 1, white. Inset shows variation in iron between the points.

Brown

Comparing the brown of point 8 with the red-orange of point 5, the brown has higher levels of manganese, calcium, and iron (figure 117). These are the signature signs of raw and burnt umber, wherein natural dirt with a high manganese dioxide content are calcified, which changes the ferric-hydrate content into ferric oxide (Wehlte 1967, 114).

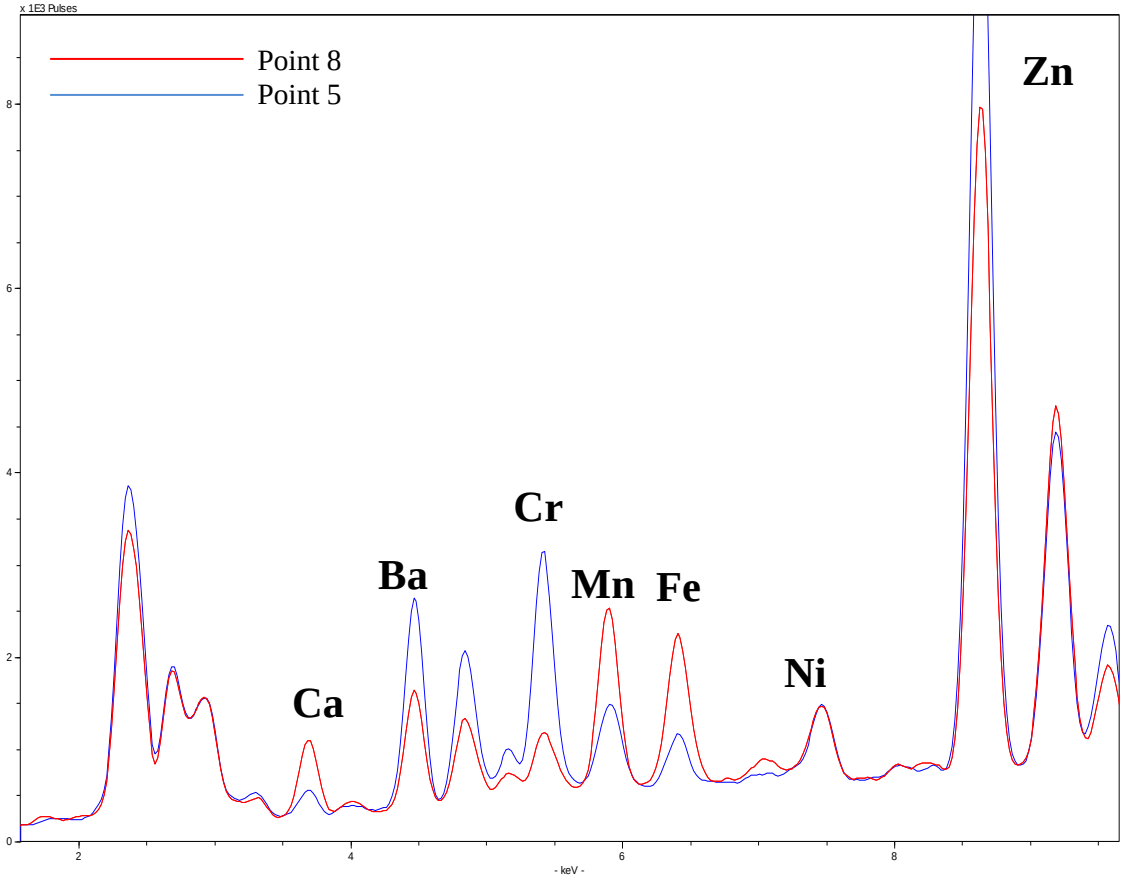

Figure 117. *Pastoral with Lady in Red*. Points 7, 10, and 11, blues, compared to point 1, white. Inset shows variation in iron between the points.

Green

Point 9 is the green of the grass to the right side of the painting. There are some slight red and yellow highlights in the grass, represented here as the zinc signature for the yellow, and the mercury for the red (figure 118). Other than these blended elements, this pigment is overwhelmingly chromium green.

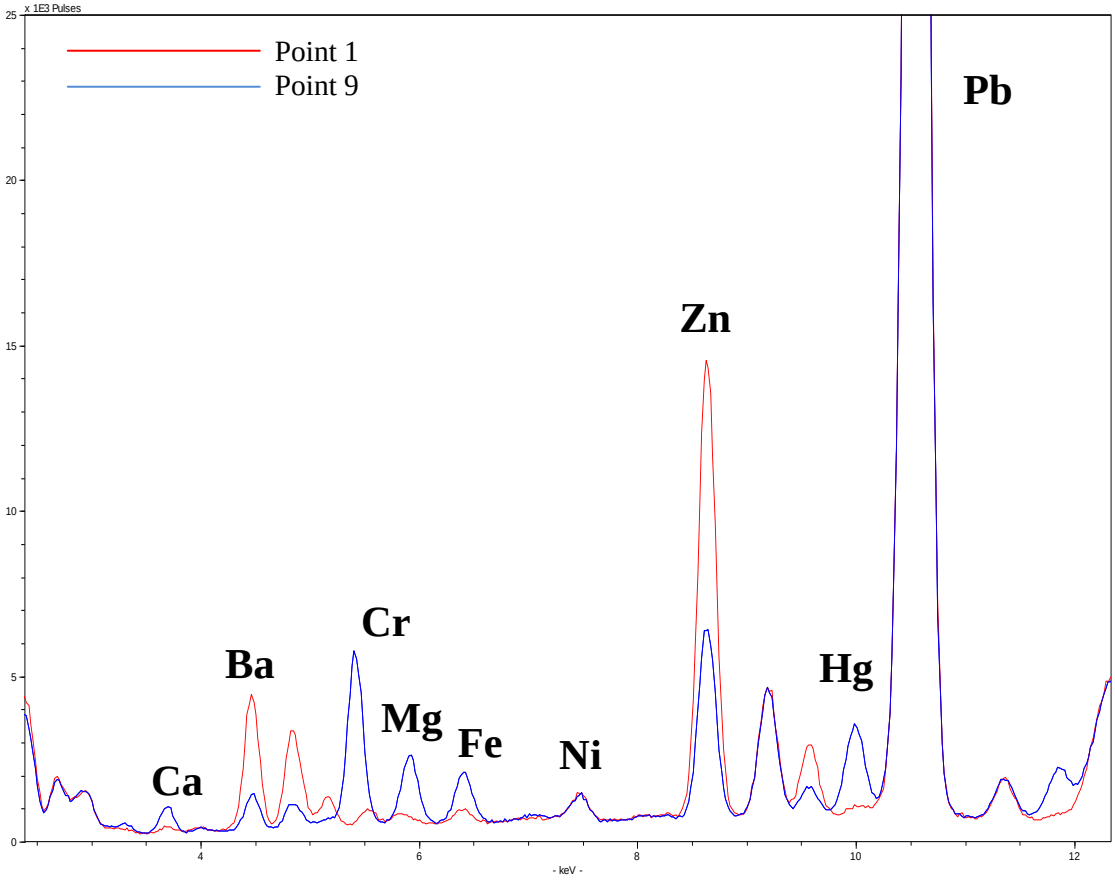

Figure 118. *Pastoral with Lady in Red*. Point 9, green, compared to point 1, white.

Seascape V

Figure 119. *Seascape V*. No Date, Signed Chas Turner, Oil on Canvas, 14in x 20in, James and Kimel Baker Collection, College Station, TX.

For *Seascape V* (figure 119), signed Chas Turner, a total of ten points were analyzed. Points 1-5 are whites, point 6 is the beige of the sail, point 7 is the brown of the rocks, point 8 is the blue green of the water, point 9 is the blue of the sky, and point 10 is the signature.

White

All five of the whites, points 1-5, are lead based whites with a strong zinc element, which probably indicates the brighter zinc white used for highlights (figure 120). The barium peak might indicate the use of *blanc fixe*, a barium sulfate white introduced around 1830 that is known to be a particularly brilliant white (Wehlte 1967, 69)

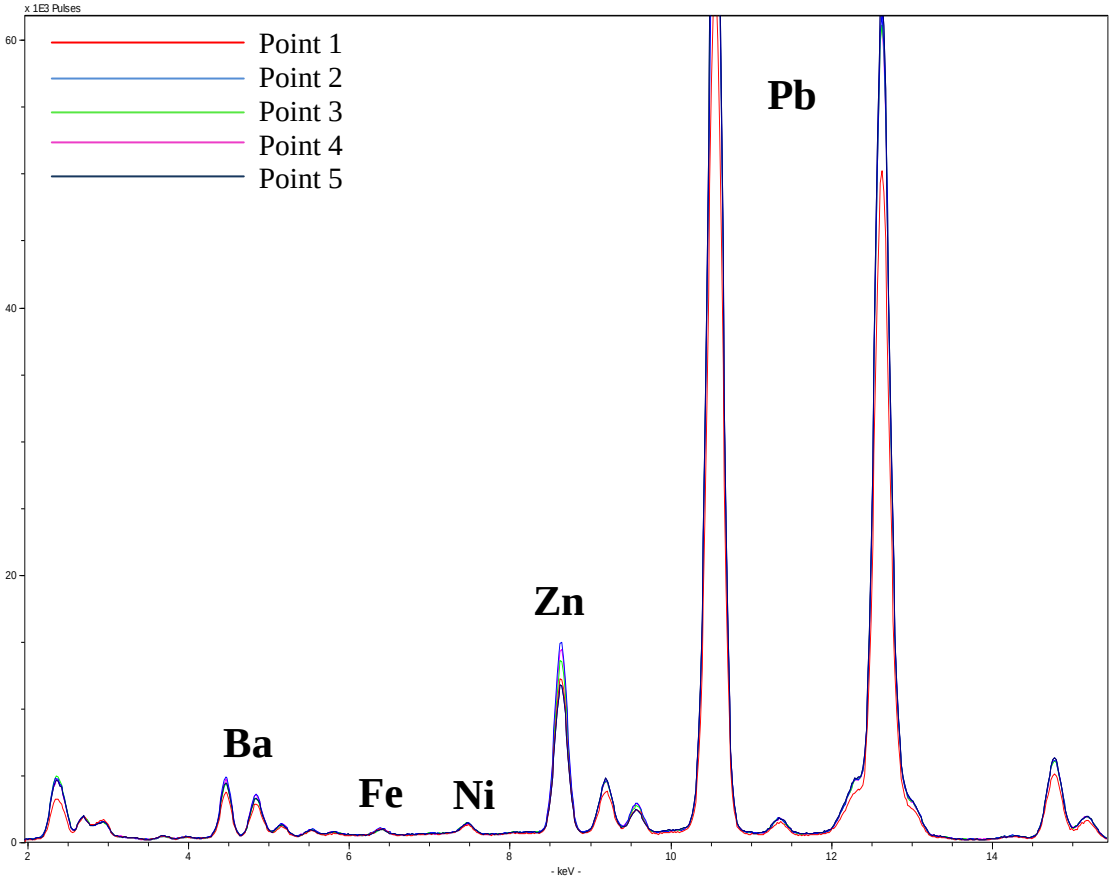

Figure 120. *Seascape V*. Points 1-5, whites.

Beige

The sail of the boat poking above the horizon, point 6, is a beige or off-white color. Compared to the white of point 1, the only difference is a slightly elevated iron peak, so it is likely an ochre mixed in with the white to give it the beige color (figure 121).

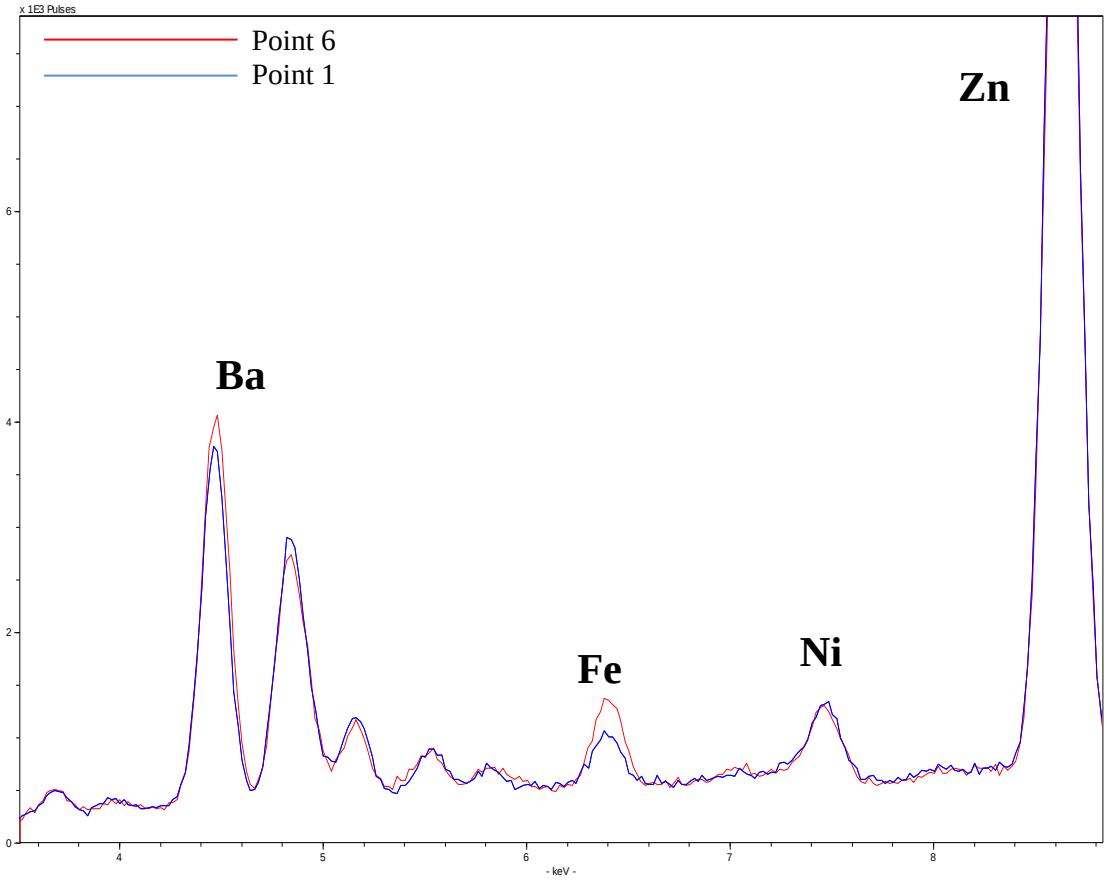

Figure 121. *Seascape V*. Points 1, white, compared to point 6, beige.

Brown and Red

Point 7, the reddish brown rocks on the left of the painting, is set apart from the whites and beige of points 1-6 by its high mercury, iron, and slightly elevated calcium content (figure 122). The mercury indicates vermillion red, and the iron and calcium are likely ochre.

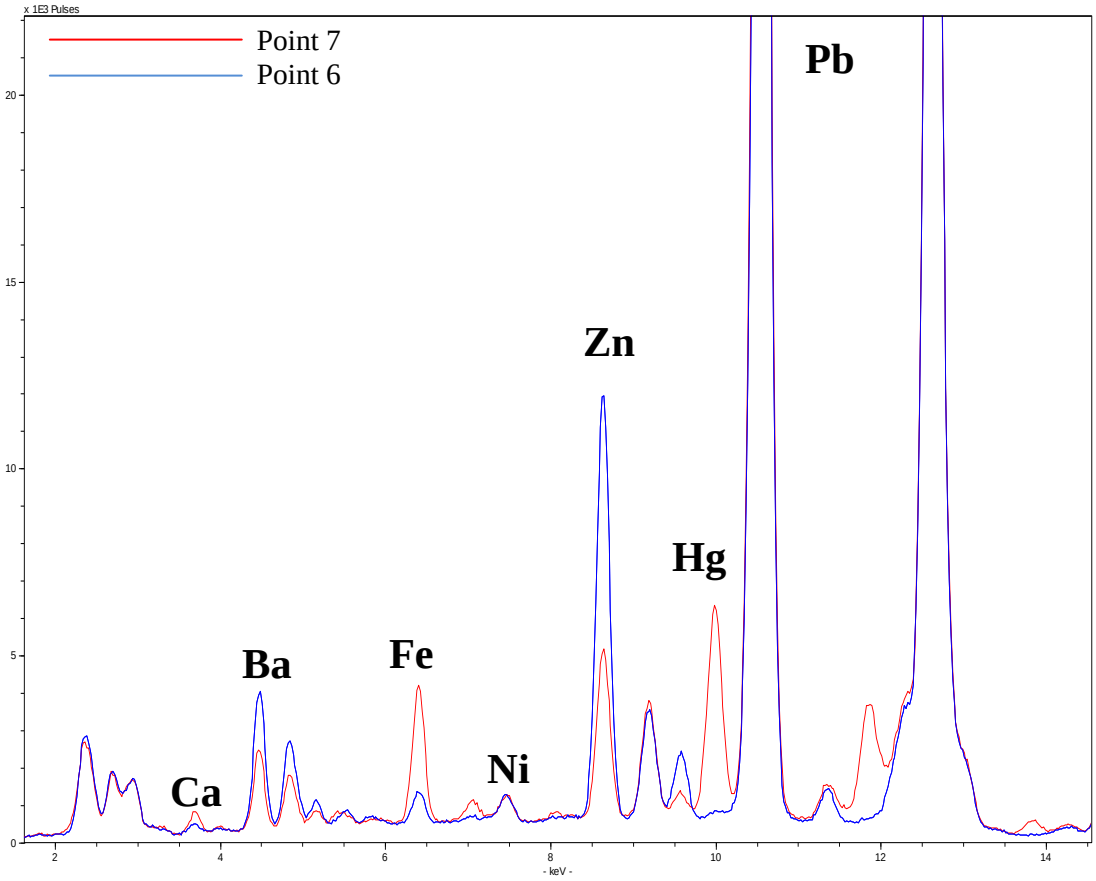

Figure 122. *Seascape V*. Point 7, brown, compared to point 6, beige.

Blue and Green

Point 8 is the blue green of the sea water, and point 9 is the blue of the sky. It is useful to compare and contrast these two to determine which elements represent blue pigments and which represent green. The spectrum for the blue-green point has mercury, which the sky does not have, as well as chromium, and a slighter elevated energy spike for iron (figure 123). The blue for the sky is nearly identical to white of the sky, once again indicating an organic blue pigment, like indigo. The mercury in the sea is from red vermillion, and the chromium is from viridian green.

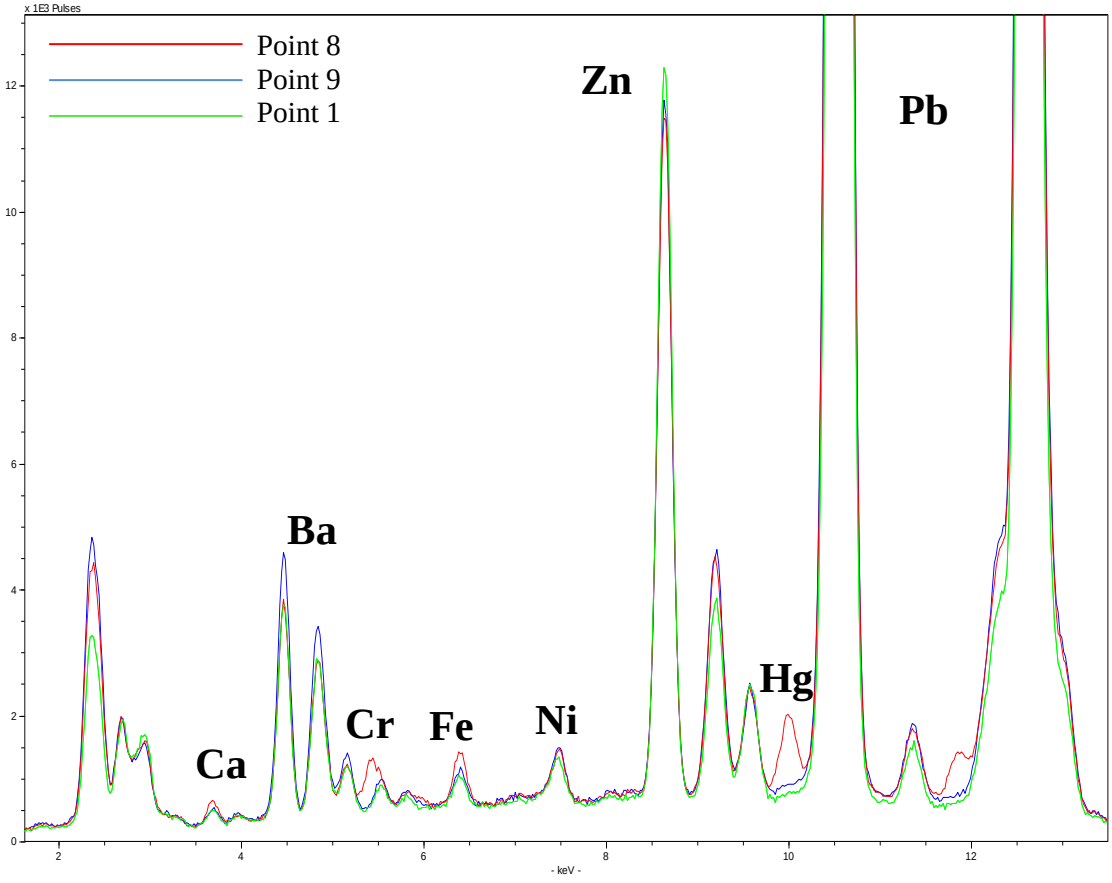

Figure 123. *Seascape V*. Points 8 and 9, blues, compared to point 1, white.

Signature

The signature, point 10, compared to point 5, the white of the sea just to the left of it, shows an elevated peak at mercury, iron, zinc, and calcium (figure 124). This indicates that the dark pigment used to sign the painting was a blend of ochre and vermillion red, very similar to the colors used to paint the rocks of point 7.

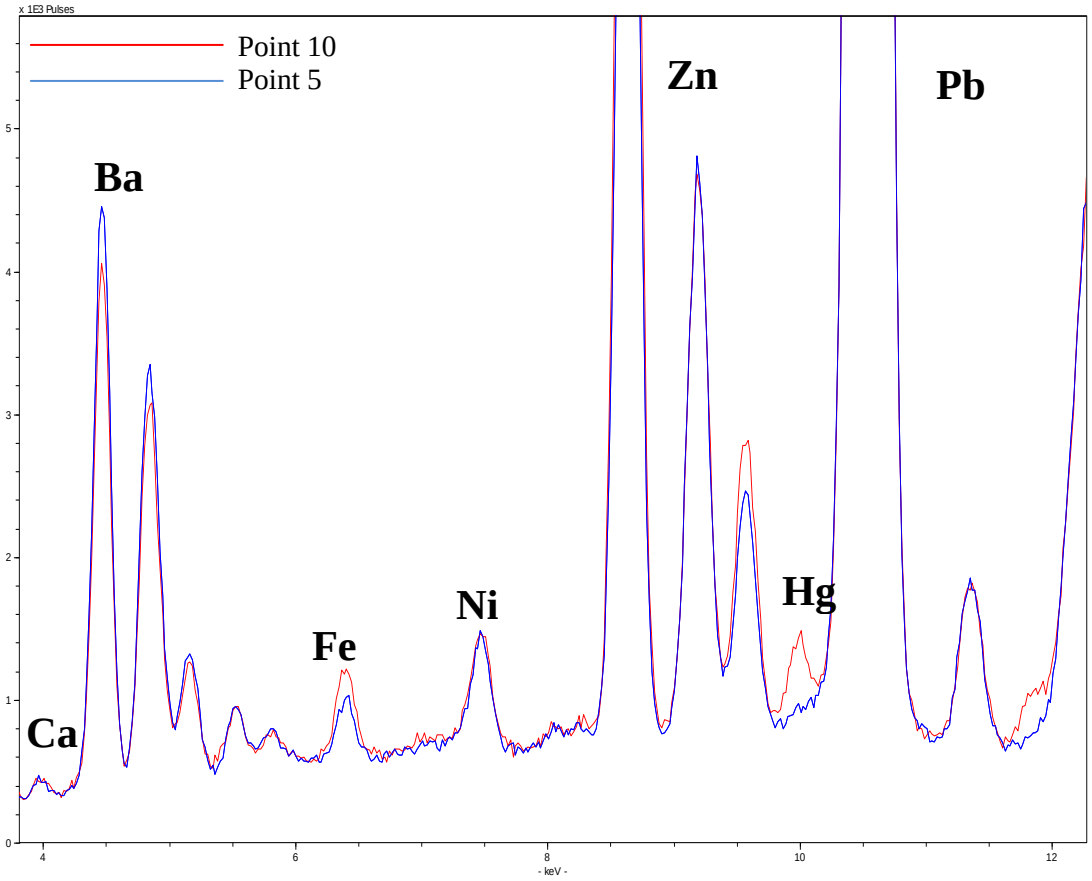

Figure 124. *Seascape V*. Point 10, the signature, compared to point 5, white.

Landscape with Cacti

Figure 125. *Landscape with Cacti*. No Date, Signed Julian Onderdonk, Oil on Canvas, 14in x 20in, James and Kimel Baker Collection, College Station, TX.

A total of nine points were analyzed for *Landscape with Cacti* (figure 125). Point 1 is the red of a flower, point 2 is the yellow of a flower, point 3 is a light green highlight in the grass, point 4 is the orange of a flower, point 5 is the green of a cacti leaf, point 6 is a white spot in the road, point 7 is the blue of the mountains, point 8 is the background of the signature and point 9 is the signature.

Red, Orange, and Signature

Point 1, the red of a flower, point 4, the orange of a flower, and points 8 and 9, the signature and background of the signature all have similar compositions. These four points, when compared to the rest of the spectra, have considerably higher peaks for lead (figure 126). This indicated that the reds in this painting are either minium (Pb_3O_4), or litharge (PbO). Along with this, it is likely that an organic based red is used, as the lead peak for the vivid red of point 1 is smaller than that of points 4, 8, and 9.

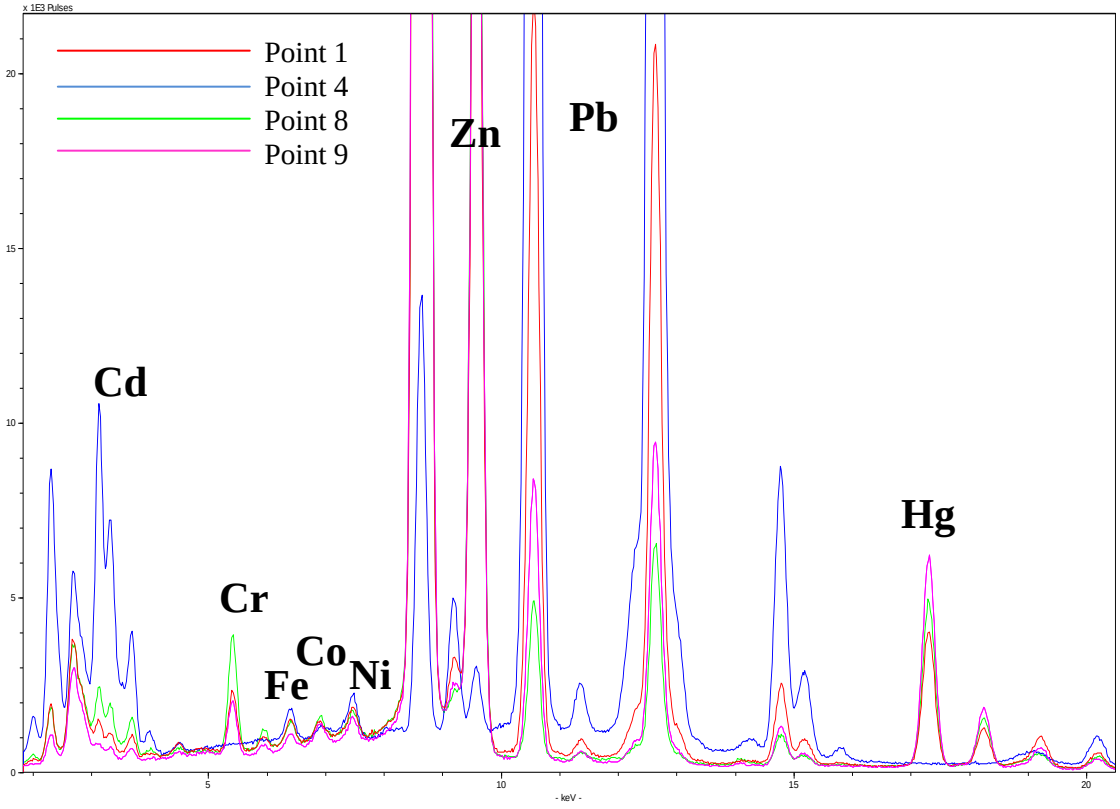

Figure 126. *Landscape with Cacti*. Point 1, red, compared to point 4, orange, and point 8 and 9, the background and the signature.

Yellow and White

Point 2, the yellow of a flower, has a distinct cadmium and sulfur peak, clearly indicating the use of cadmium yellow (figure 127). When comparing the yellow to the white of point 6, it becomes clear that the lead is not contributing to white in this particular painting. This is a zinc white (ZnO), and the painting was likely primed with this as well. The only other distinct peak in the white spectra is the sum peak for zinc.

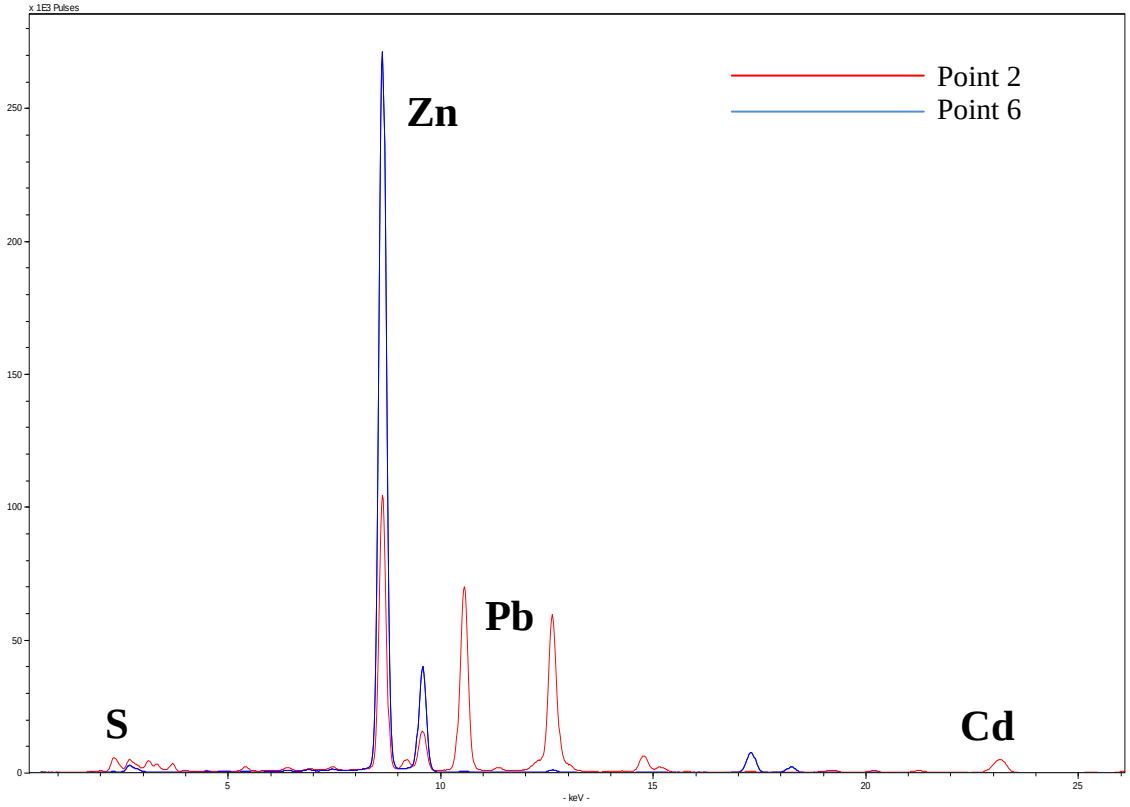

Figure 127. *Landscape with Cacti*. Point 2, yellow, compared to point 6, white.

Green

As seen in figure 128, the different hues of green from this painting, points 3 and 5, are both characterized by their strong chromium peak, indicating emerald green, or chromium oxide (CrO3) . Point 5 has a higher level of lead, indicating that the green was blended with more red lead.

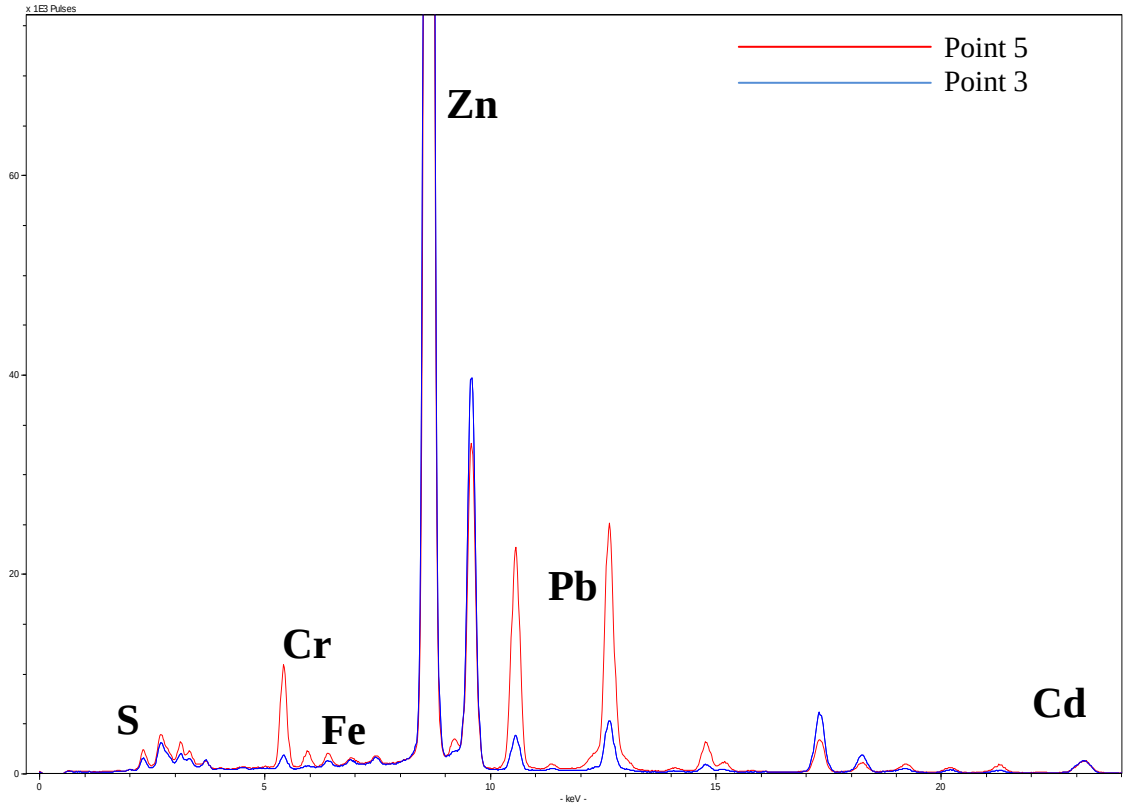

Figure 128. *Landscape with Cacti.* Points 3 and 5, greens.

Blue

The blue of the mountains in the background, point 7, has a distinct cobalt peak, but not a tin or an aluminum peak, suggesting that cobalt blue and cerulean blue were not used (figure 129). This would suggest the use of smalt, cobalt-doped silica glass that is ground up and used for pigment. There is also a distinct lead peak, indicating that violet hues are due to mixing this cobalt based blue with a lead based red.

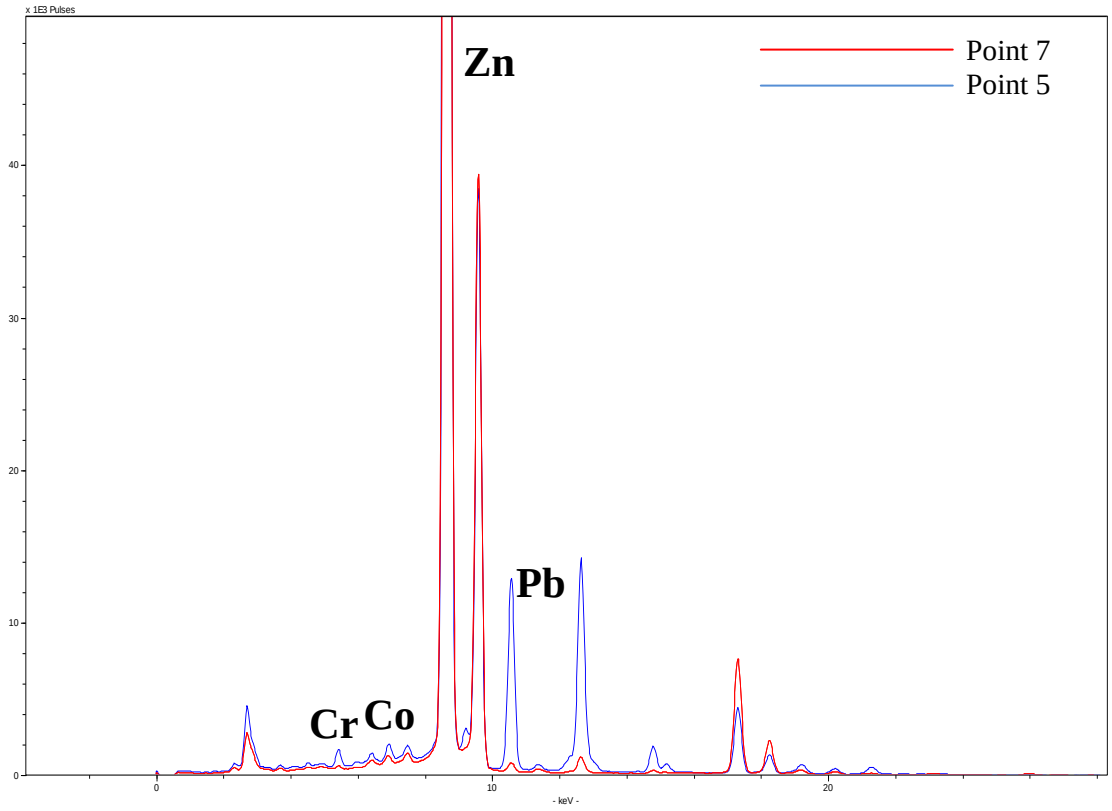

Figure 129. *Landscape with Cacti*. Points 5 green, compared to point 7, blue.

A Man Fishing from a Boat

Figure 130. *A Man Fishing From a Boat*, No Date, Signed Chas. Turner, Oil on Canvas, 14in x 20in, James and Kimel Baker Collection, College Station, TX.

A total of nine points were analyzed for *A Man Fishing from a Boat* (figure 130). Points 1-4 are whites, 5 is red, 6 is blue, 7 is green, 8 is the signature, and 9 is dark green. An atypical titanium peak from point 1 led to further examination of the painting, and under a black light it was revealed that a strip of repair had been done to the top of the painting, accounting for the titanium peak.

White

The whites pigments in *A Man Fishing from a Boat*, points 2, 3, and 4 are three very similar lead based white pigments with some zinc and barium, both of which were used as other sources of white pigment at the time, along with varying trace amounts of iron, copper, and tin (figure 131). The white in point 1 was inconsistent with these other 3 points, being largely titanium based (figure 132). Titanium as a white pigment was first introduced in 1795 as TiO2, (Artoli 2010, 269), but it was not introduced as a pigment for paint manufacture until 1921 (Douma 2008), and not available in artists paints until the later 1920s - early 1930s. This small section was clearly not painted by Onderdonk, but given that the rest of the whites in the painting are lead based, it seems likely that this area represents a modern restoration attempt, and is not indicative of any overall inauthenticity in the painting (figure 133).

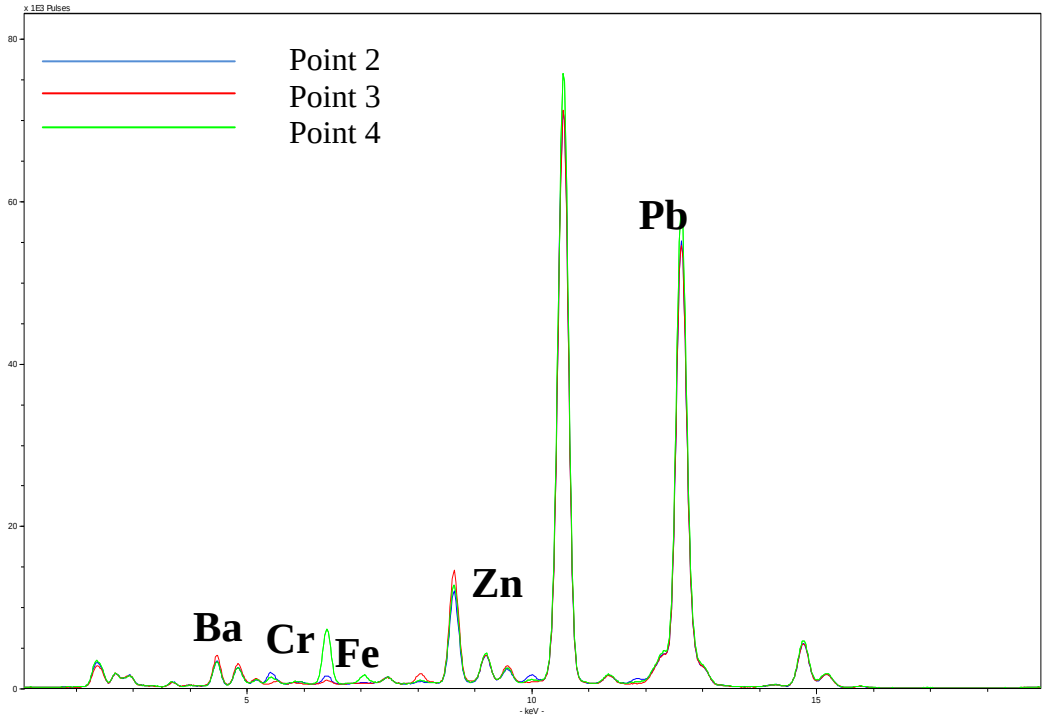

Figure 131. *A Man Fishing From a Boat*. Points 2, 3, and 4, whites.

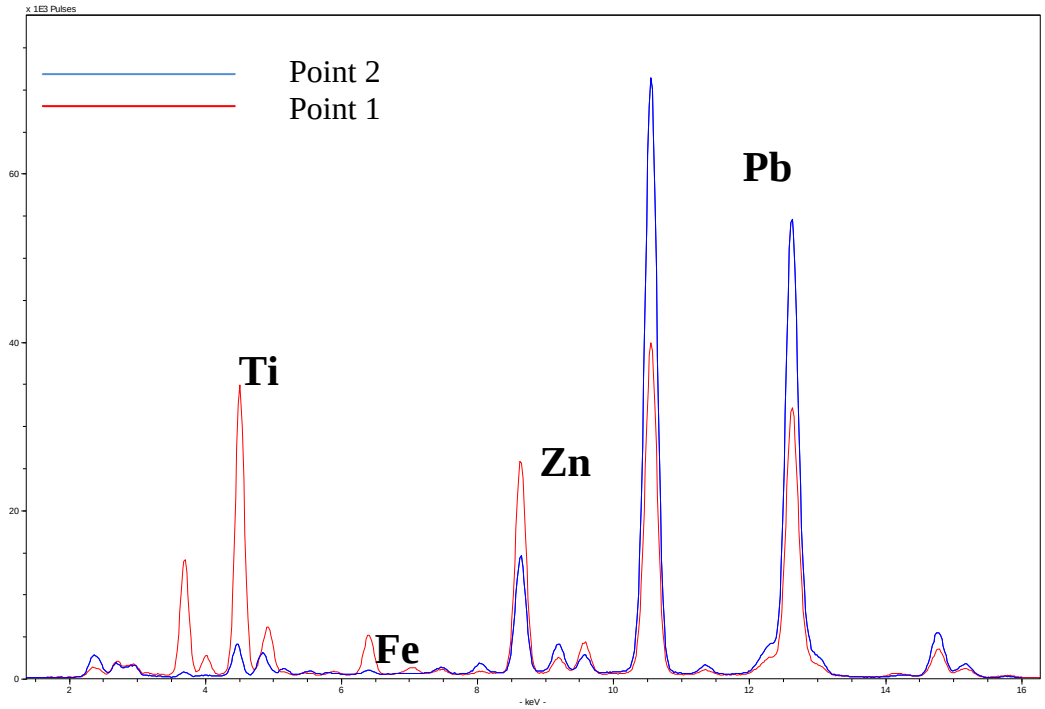

Figure 132. *A Man Fishing From a Boat*. Point 1, white with titanium, and 2, white without titanium.

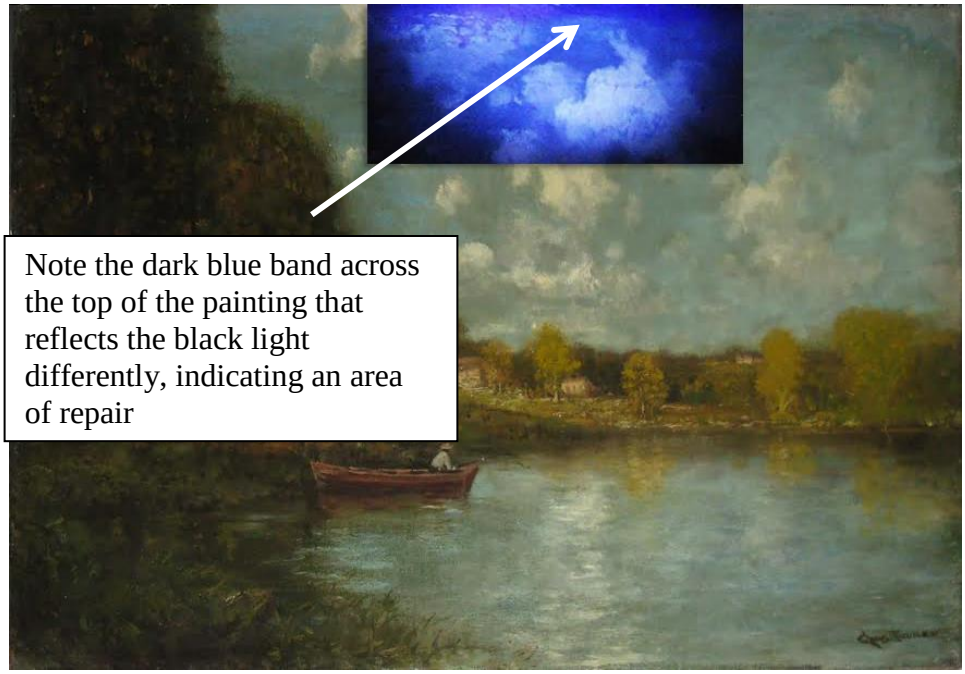

Figure 133. *A Man Fishing From a Boat*. Black light evidence of restoration. Photo courtesy of James Baker.

Red

Point 5, the red in the hull of the boat, is very similar in composition to the white points 2-4, with a higher level of iron, suggesting a hematite (Fe_2O_3) or ochre (Fe^{+3} with clay and quartz) based pigment (figure 134).

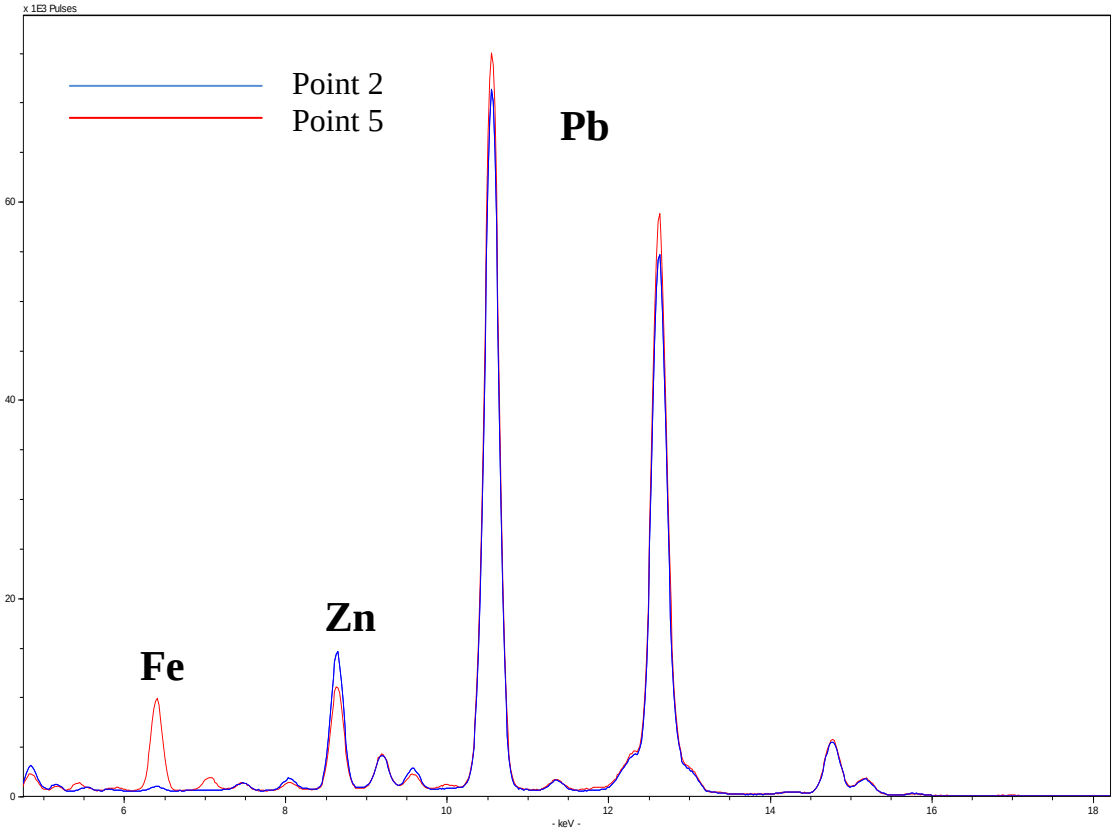

Figure 134. *A Man Fishing From a Boat*. Black light evidence of restoration attempt.

Blue

Point 6 is the blue of the water, and compared to the white there are elevated levels of copper and iron (figure 136). This could indicate that the blue was azurite ($Cu_3(CO_3)_2(OH)_2$), Egyptian blue ($CaCuSi_4O_{10}$) or, given its popularity in the 19th century, Prussian blue ($Fe_4[Fe(CN)_6]_3$). All of these variants were readily available to Onderdonk in the late 19th and early 20th centuries.

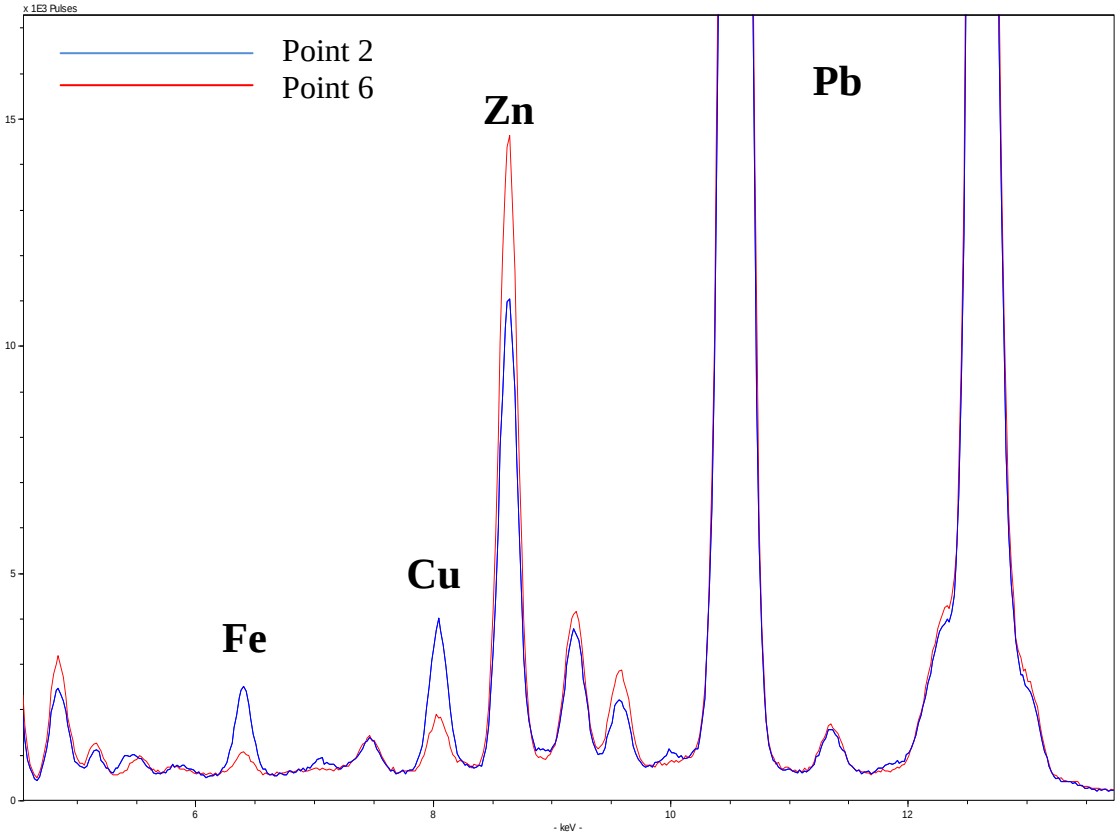

Figure 135. *A Man Fishing From a Boat*. Point 6, blue, compared to point 2, white.

Light Green

Point 7 is the green of the tree on the right side of the painting, and while it is likely mixed with some yellow or white to achieve the hue it has, the green is almost certainly the result of chromium oxide (Cr_2O_3). Interestingly, there are also elevated levels of calcium and mercury in this point, and mercury is generally only seen in pigments in the red form of cinnabar (figure 136).

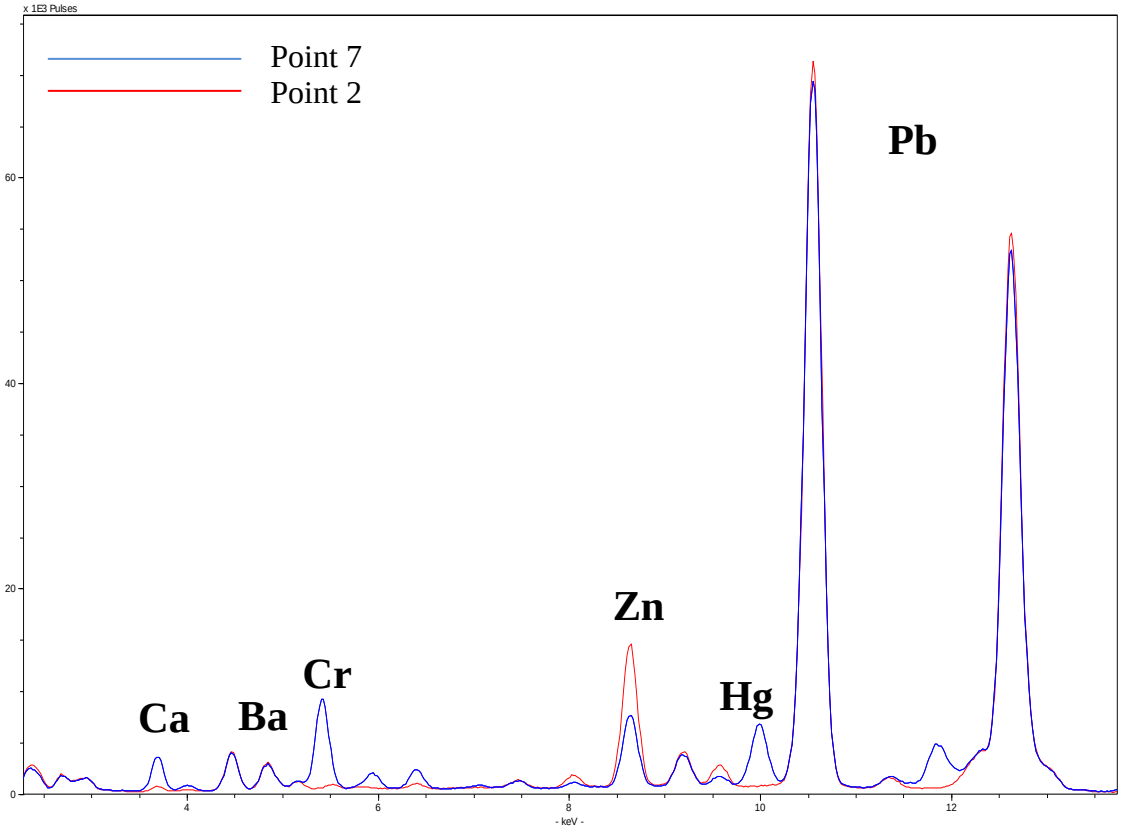

Figure 136. *A Man Fishing From a Boat.* Point 7, green, compared to point 2, white.

Signature

Point 8 is the signature. Overlaying the signature with the blue from the water shows that the only significant difference between the two points is that the level of copper is higher in point 8 (figure 137). This indicated the addition of a copper based blue.

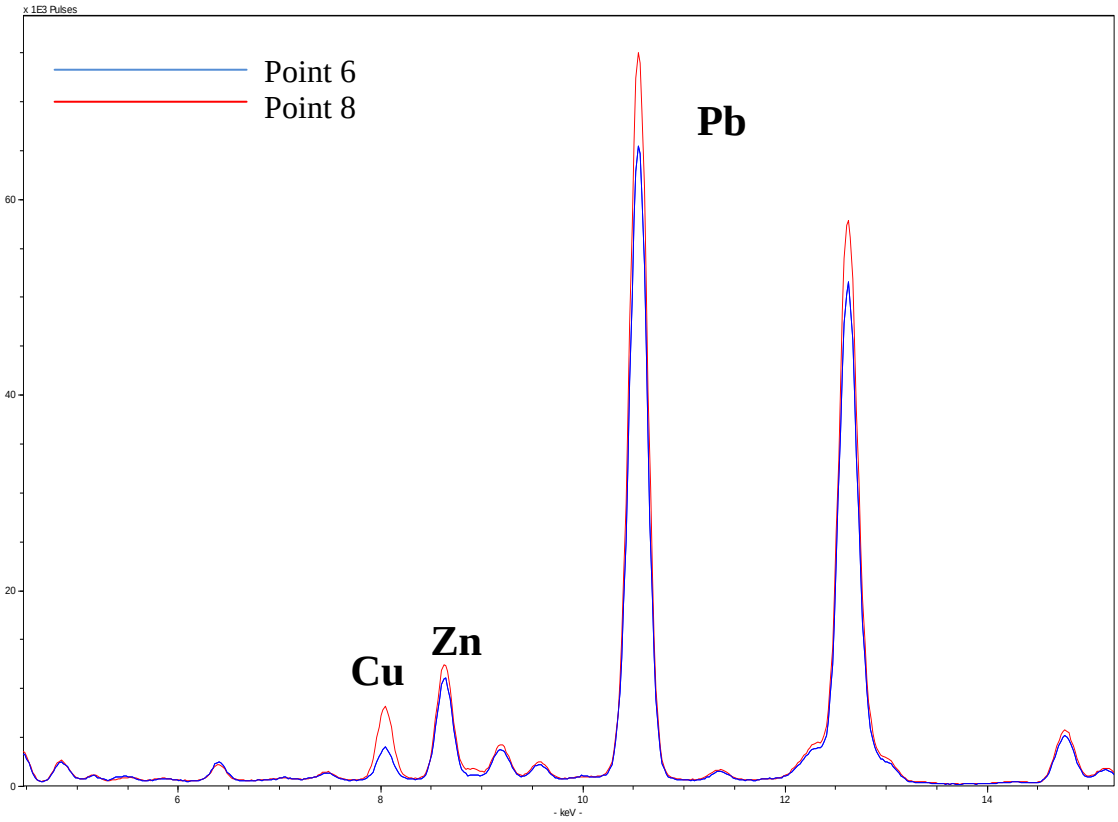

Figure 137. *A Man Fishing From a Boat*. Point 8, the signature, compared to point 6, blue.

Dark Green

Finally, point 9 of this painting is the dark green of the shaded grass below the trees on the left hand side of the scene. Compared to the lighter green of the tree to the right side of the painting, point 7, the dark green, contains more iron, less chromium, less barium, and less zinc (figure 138). The difference in barium and zinc content is likely due to the lightening component added to point 7, and the decrease in chromium (green) and the increase in iron (red) is indicative of a blend of both to achieve the darker color green in point 9.

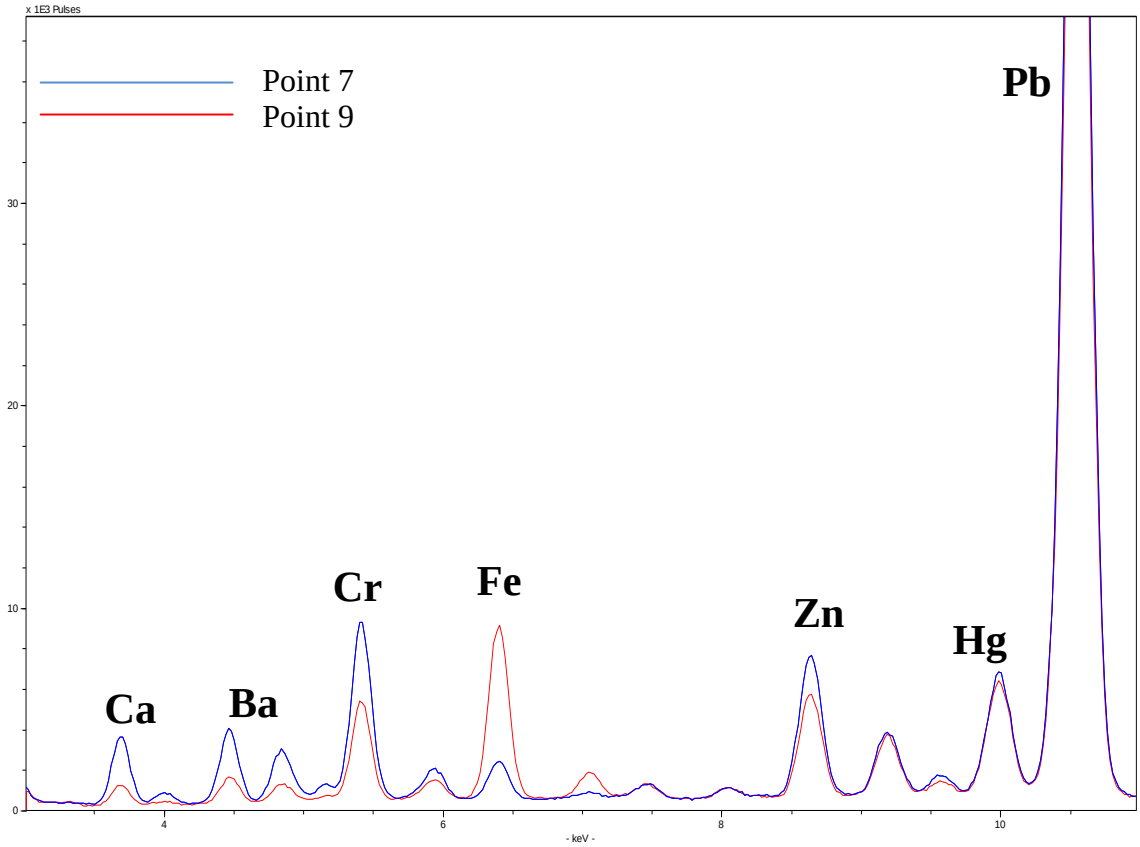

Figure 138. *A Man Fishing From a Boat.* Point 9, dark green, compared to point 7, light green.

At the Edge of the Forest

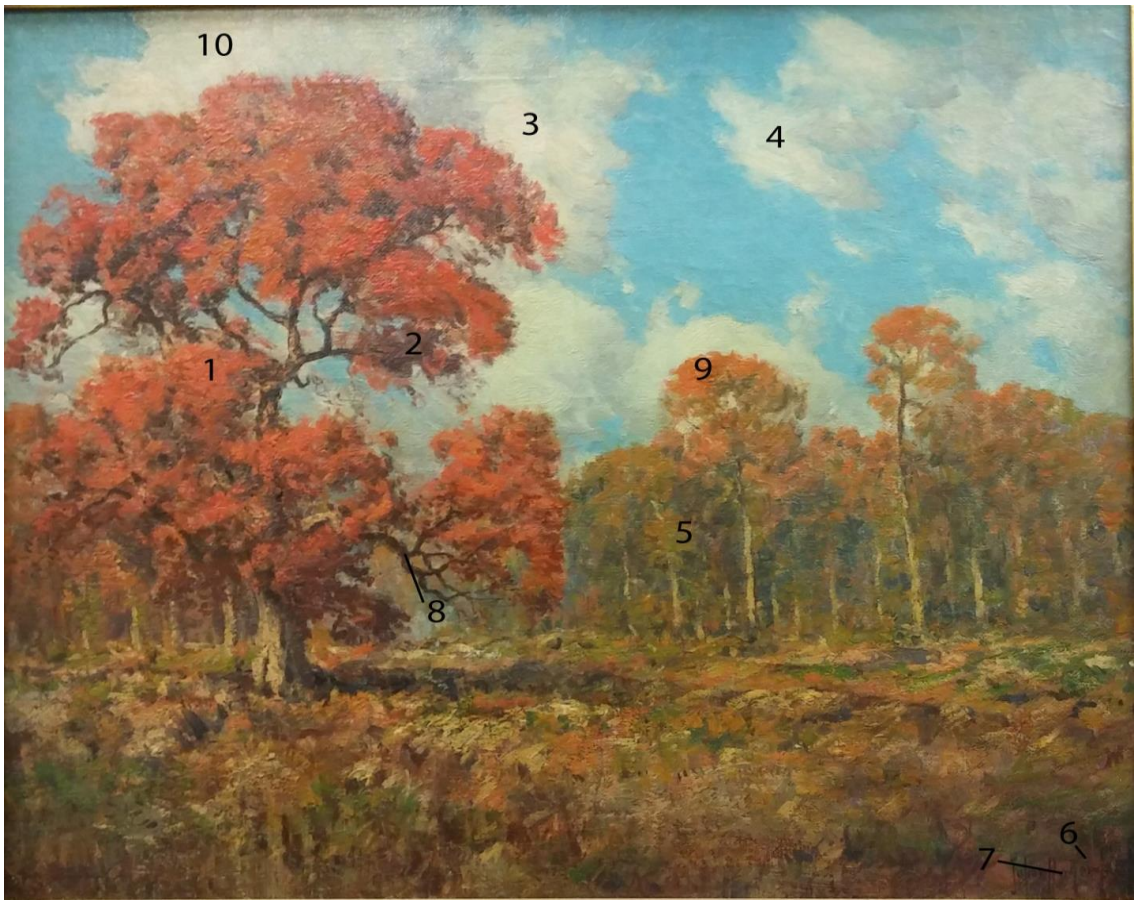

Figure 139. *At the Edge of the Forest*. No Date, Signed Julian Onderdonk, Oil on Canvas, 22in x 22in, Stark galleries, Texas A&M University.

A total of ten points were analyzed for *At the Edge of the Forest* (figure 139). Points 1, 2, 8, and 9 are hues of red and orange from the trees, points 3, 4, and 10 are the whites of the clouds, point 5 is the green of the trees, and points 6 and 7 are the area around the signature and the signature itself, respectively.

Red and Yellow

Points 1 and 2 are red, while point 8 is more of a reddish brown, and point 9 is an orange hue. There are 2 main pigment sources bringing the red color, mercury based vermillion, and iron based hematite or ochre (figure 140). The vibrant reds appear to be vermillion, while the darker earthier tones are iron based. Based on the composition of point 8, the brownish red of the tree trunk, and point 9, the orange of the leaves, both of these points were mixed with yellow pigment, which given the peaks for zinc and chromium in point 8, and the peaks for cadmium and sulfur in point 9, are both zinc yellow (ZnCrO4) and cadmium yellow (CdS).

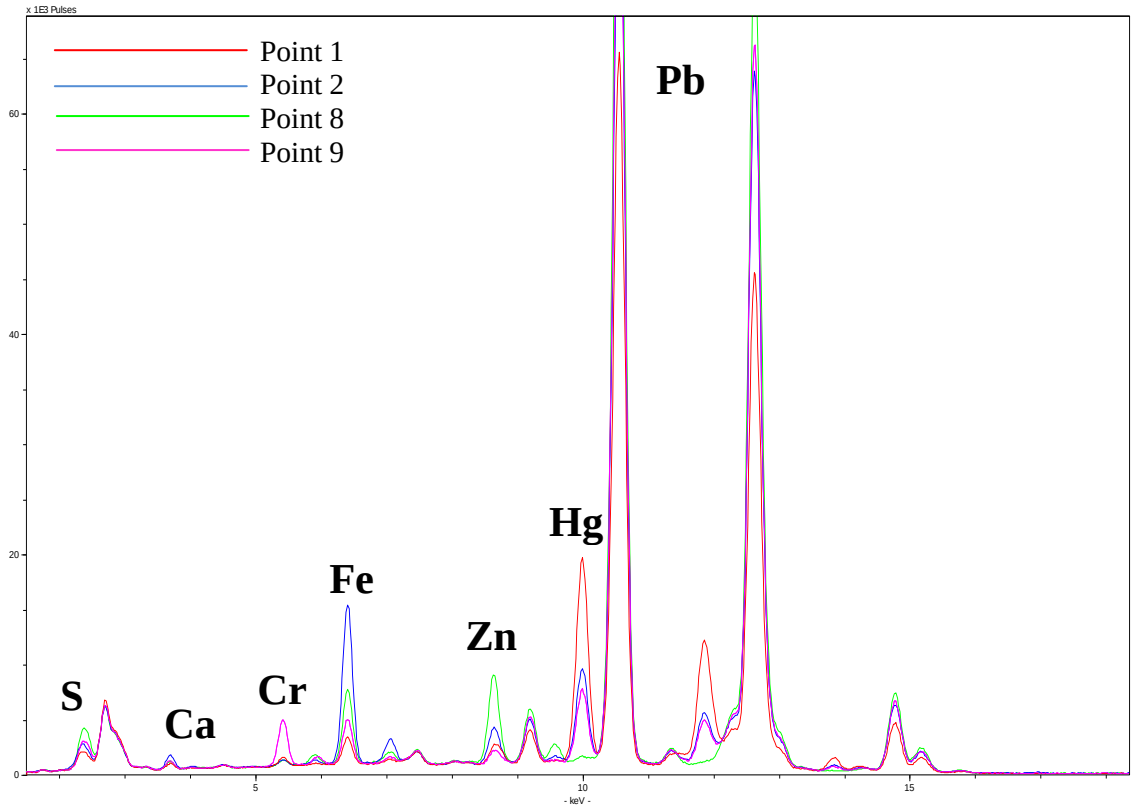

Figure 140. *At the Edge of the Forest*. Points 1, 2, 8, and 9, all hues of red and orange.

White

Points 3, 4, and 10, the whites of the clouds in the sky are predominantly lead-based. However, point 3 and 10 have peaks for titanium, and point 3 has a higher peak for zinc (figure 141). The zinc is likely from zinc yellow, but the titanium is again problematic. The spectral patterns of the pigments in this painting, (apart from the titanium), are closer to those of Onderdonk's early works, not his later works. It would appear that both Onderdonk paintings in the Stark galleries were restored using titanium white. As noted before, this means that the spectral signatures of the other pigments cannot be relied upon to associate this painting with others with known dates.

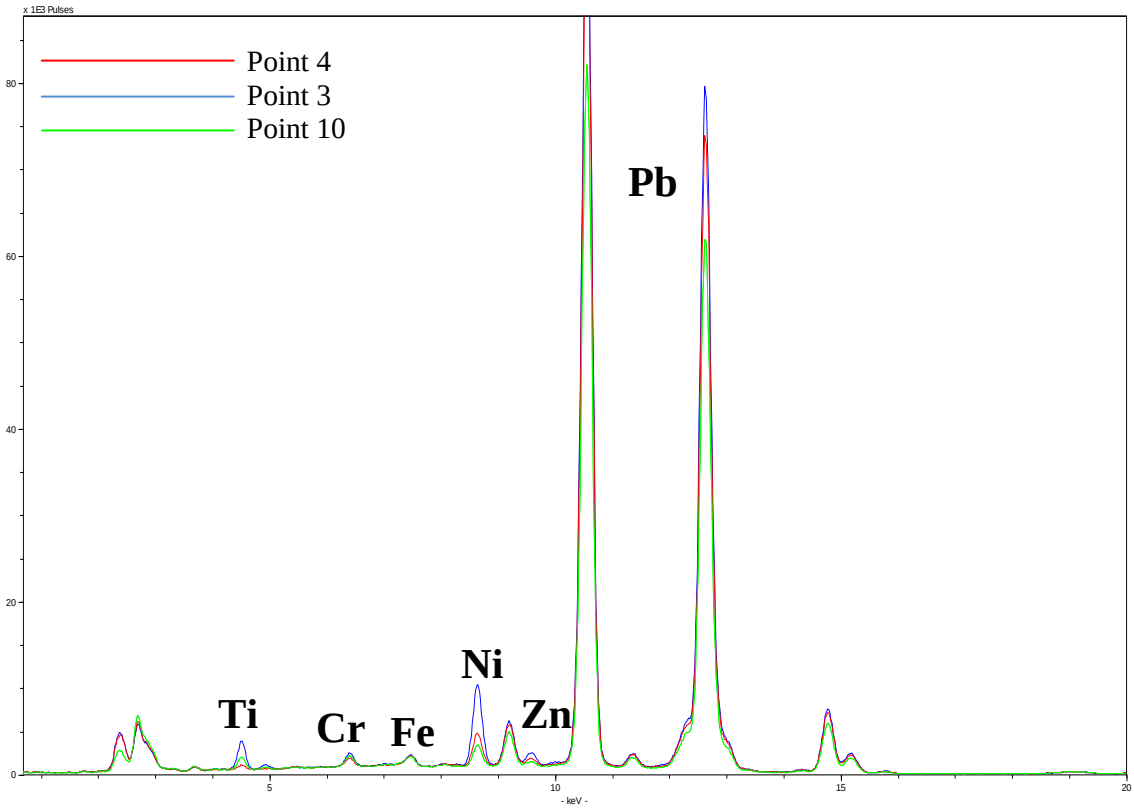

Figure 141. *At the Edge of the Forest*. Points 3, 4, and 10, whites.

Green

The green of point 5 has peaks for chromium, mercury, and a very slight peak for copper (figure 142). The chromium peak is higher than the zinc peak, so it is unlikely that the chromium is accounted for by zinc yellow. Instead, it is most likely that the green is chromium oxide, or emerald green. The trace of copper could represent the presence of a copper based green pigment, but the peak is so subdued compared with the copper-based greens seen in the other works that it seems unlikely to be the case.

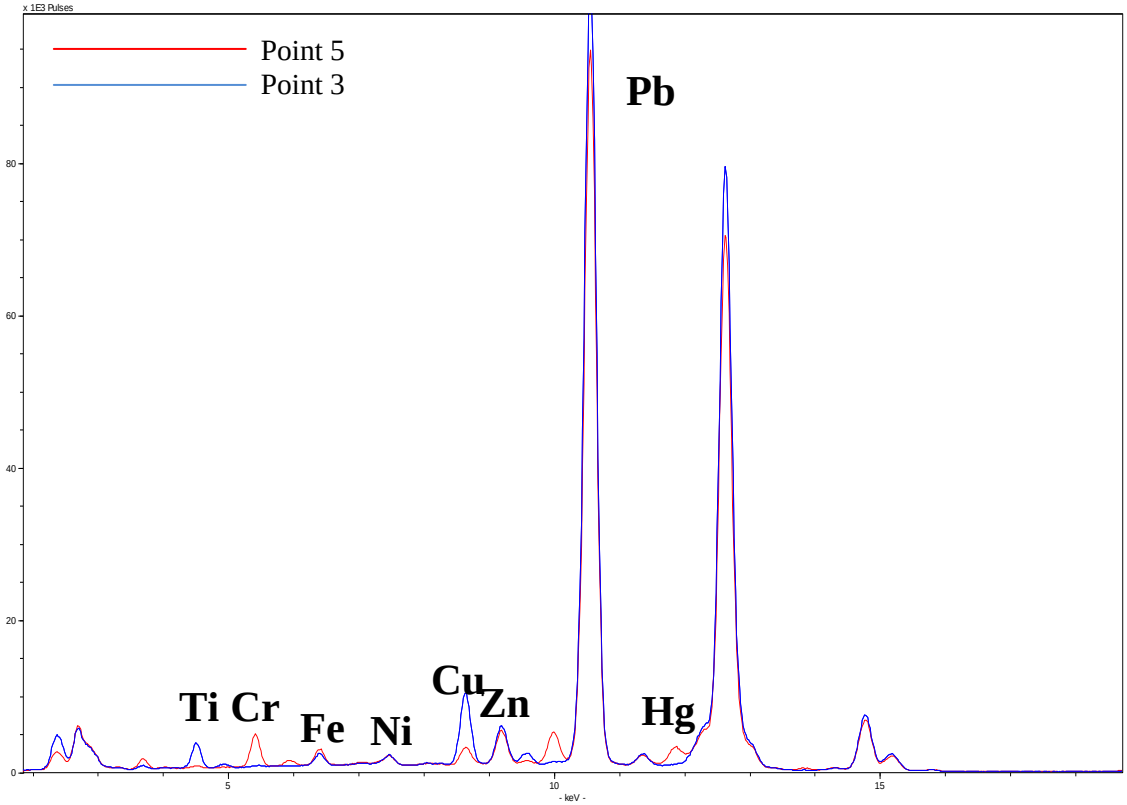

Figure 142. *At the Edge of the Forest*. Point 5, green, compared to point 3, white.

Signature

Like the reds and browns of the tree in point 2, points 6 and 7, the background and the signature, are an iron based ochre or hematite (figure 143).

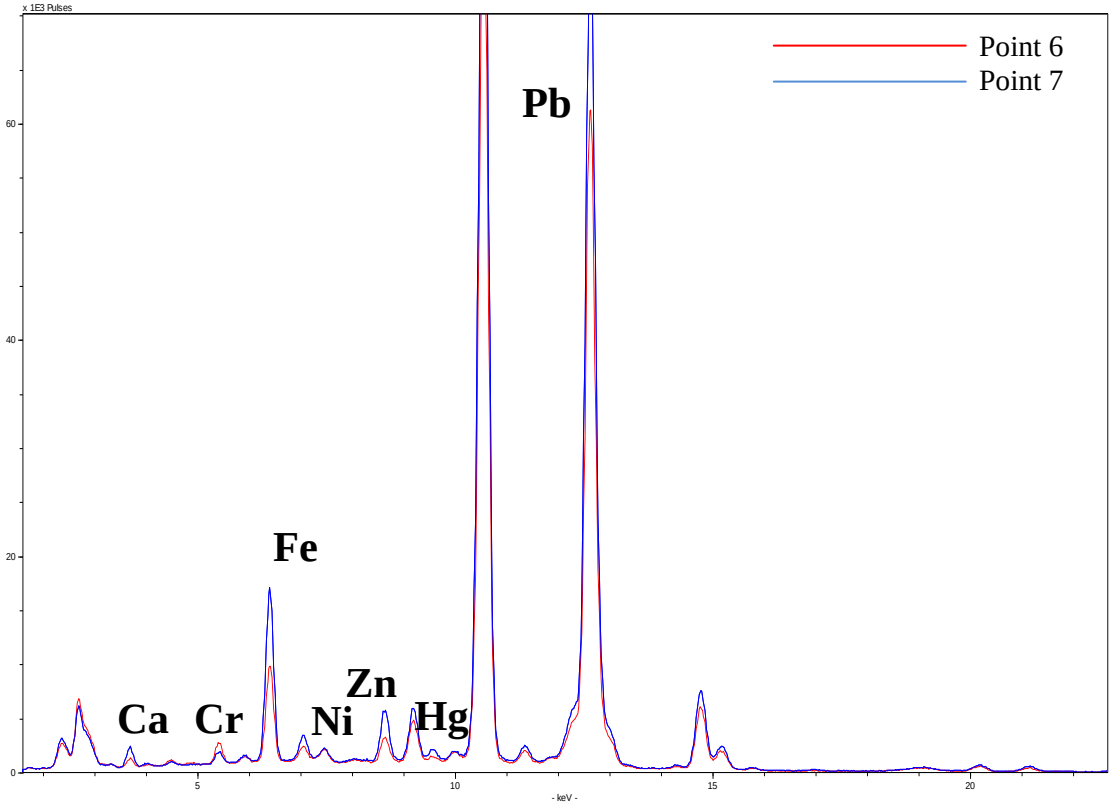

Figure 143. *At the Edge of the Forest*. Point 6 and 7, the background and the signature.

Bluebonnets in San Antonio

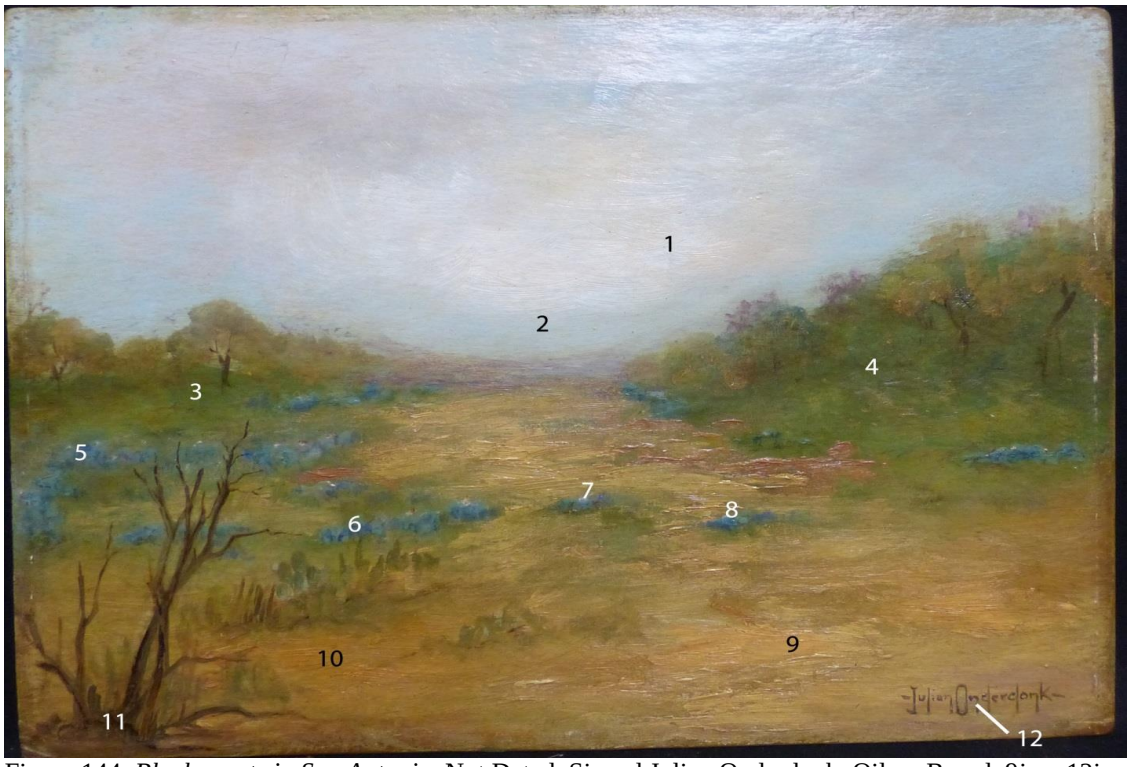

Figure 144. *Bluebonnets in San Antonio*, Not Dated, Signed Julian Onderdonk, Oil on Board, 9in x 12in, James and Kimel Baker Collection, College Station, TX.

For *Bluebonnets in San Antonio* (figure 144), eleven points were analyzed. Point 1 is the white of the sky, 2, 5, 6, 7 and 8 are variants of blue, 3 and 4 are the greens of the grass and trees, 9 and 10 are the yellows of the ground, 11 is the brown of the tree, and 12 is the signature.

White

This painting stands apart from the rest of the collection due to the fact that it appears to have been primed with titanium white. Titanium white has been found in several of the other paintings in isolated areas, reflecting more recent restoration attempts. For this painting though, the titanium white is found in every single point analyzed. Given the history of the pigment, it is impossible for Julian Onderdonk to have painted this before his death. As to who actually did paint Bluebonnets in San Antonio, it is impossible to know. It could have been someone intentionally trying to profit off of Julian's reputation, or it could have been a study by another artist trying to mimic Julian's style (though the presence of a signature is somewhat suspicious).

Because of the way the sky is blended, the only definitively white spot was a small highlight on a cloud. The highest peak belongs to zinc, which, given the proximity to the yellow hues in the sky, can be either zinc white or zinc yellow. However, as mentioned above, there is a strong titanium component as well, and trace amounts of manganese, and iron (figure 145). In the other paintings with titanium whites showing up in the white areas, the titanium appears to have been the work of localized restoration efforts. In this painting, the titanium is present in every point of the painting, and going by the same standards of interpretation for the rest of the paintings in this study, it would appear that this painting was primed with titanium white, which would suggest that it is not authentic.

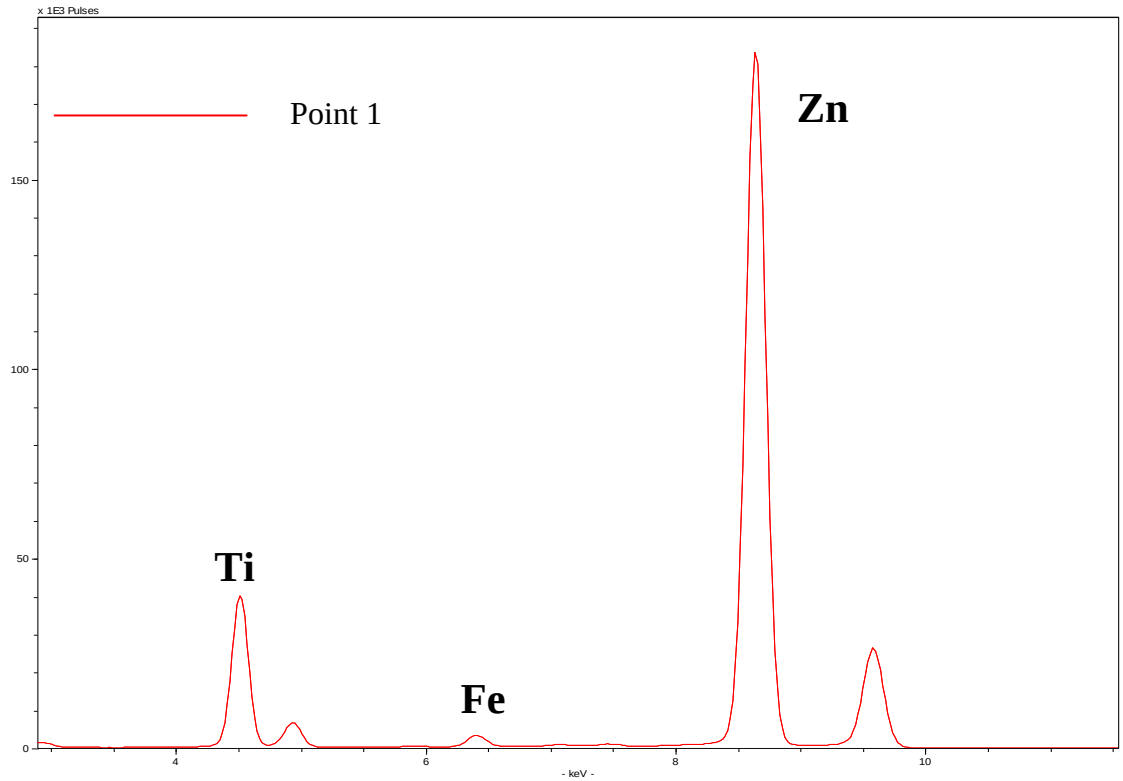

Figure 145. *Bluebonnets in San Antonio*. Point 1, white.

Blue

Points 2, 5, 6, 7, and 8 are all blue. Point 2 was taken from the blue in the sky, and 5-8 were taken from the bluebonnets. Point 2 looks very similar to the white in point 1, as would be expected in such a well-blended sky (figure 146). There is less zinc, and more iron, indicative of Prussian blue ($Fe_4[Fe(CN)_6]_3$), blended with zinc and titanium white. The blues of points 5, 6, 7, and 8 are all nearly identical. They are similar to point 2, but have more iron, less titanium, and less zinc than the sky blue, which is because point 2 is blended with the white of the clouds and points 5-8 are not (figure 147).

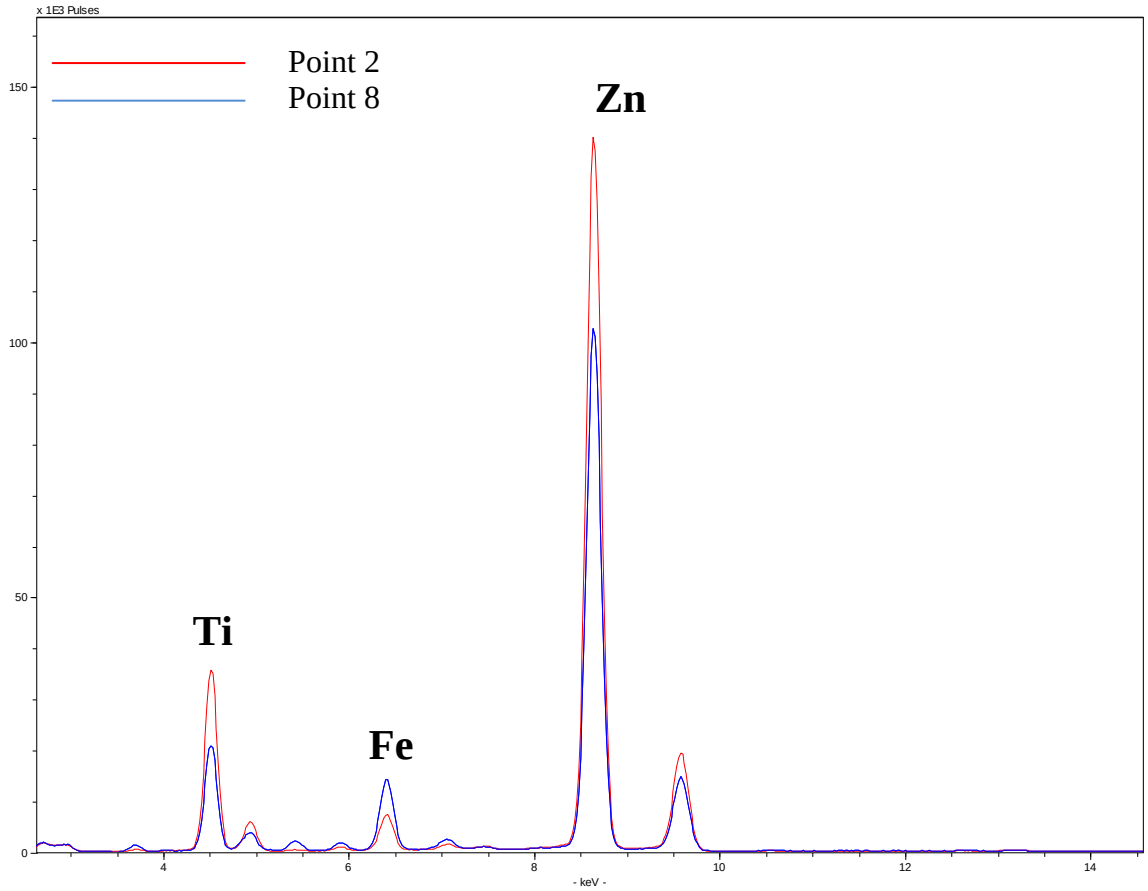

Figure 146. *Bluebonnets in San Antonio*. Points 2 and 8, blues.

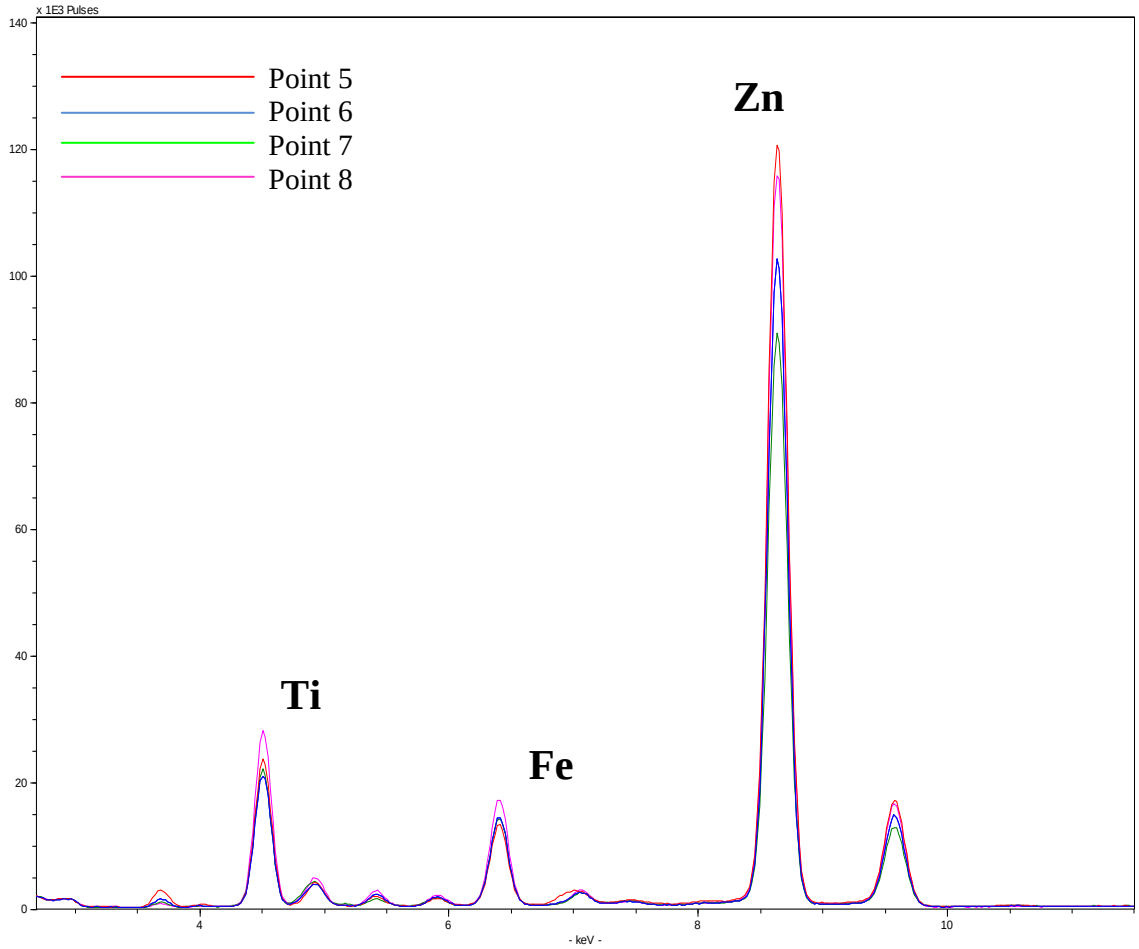

Figure 147. *Bluebonnets in San Antonio*. Points 5, 6, 7, and 8, all blues.

Green

Points 3 and 4 are both taken from shades of green that appear to be similar, and compositionally, they appear to be nearly identical. Point 3, taken from the grass on the left side of the painting, does have significantly less energy registered for zinc, iron, and titanium, but they are all there (figure 148). The appreciable difference between both greens and the rest of the pigments is the chromium levels. There is a substantial amount of chromium, which is indicative of chromium oxide, commonly known as emerald green.

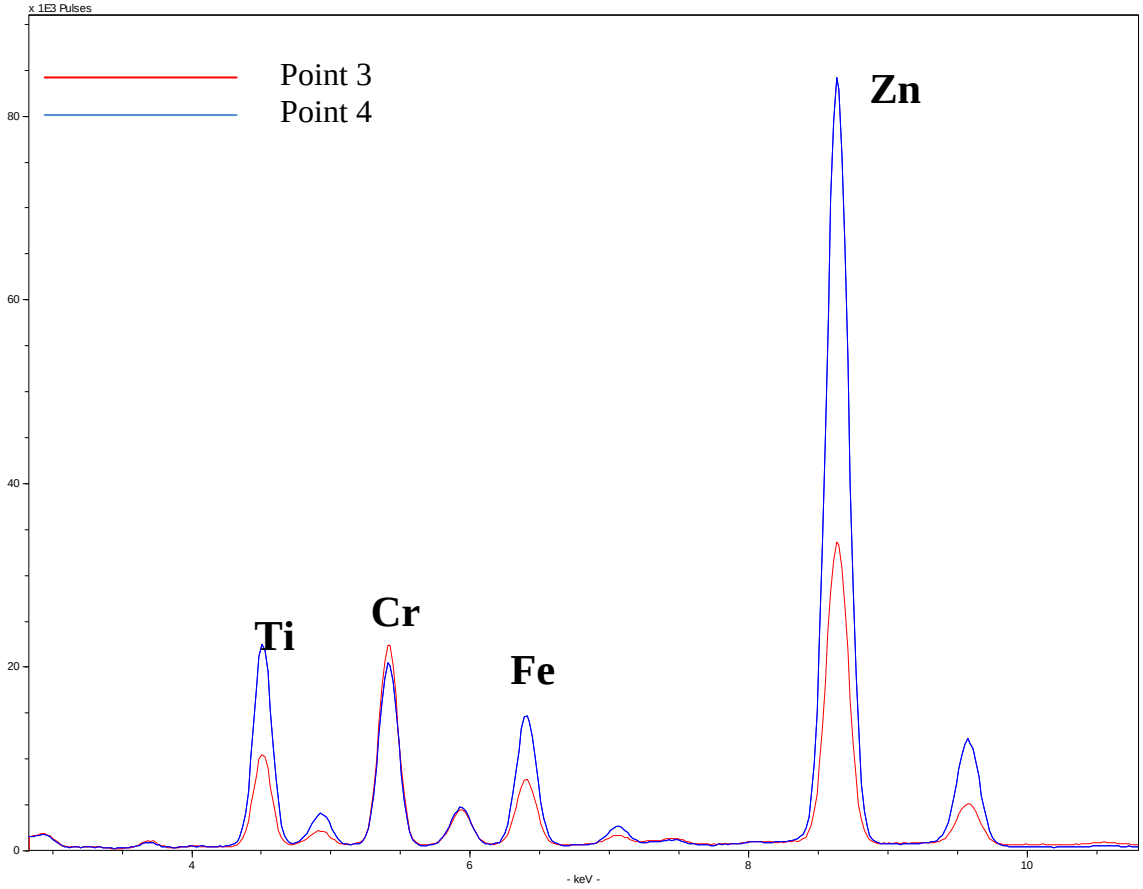

Figure 148. *Bluebonnets in San Antonio*. Points 3 and 4, green.

Yellow

The yellows of points 9 and 10 are nearly identical, and given the trace amounts of chromium and strontium, the likely pigment is lemon yellow, made with strontium chromate ($SrCrO_4$) (figure 149). However, given that the amounts of chromium and strontium are dwarfed by the zinc, iron, and titanium, it could also be zinc yellow ($ZnCrO_4$). Both lemon yellow and zinc yellow were first produced in 1809.

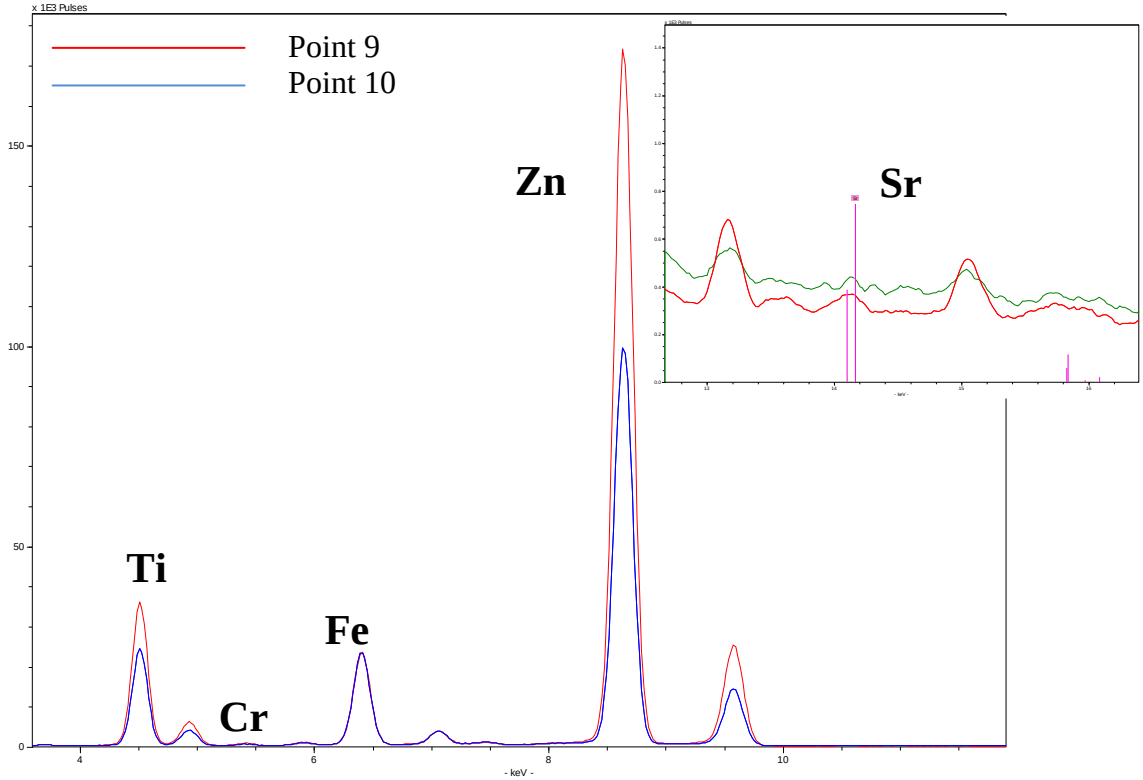

Figure 149. *Bluebonnets in San Antonio*. Points 9 and 10, yellows. Inset shows 13-15keV.

Brown

Point 11 is the brown trunk of the tree, which was clearly painted over the yellow behind it. As seen below in figure 150, given the higher level of iron, manganese, and calcium, it is likely that the brown used is a raw or burnt umber, a natural dirt with a high manganese dioxide content that is calcified, which changes the ferric-hydrate content into ferric oxide and results in a variety of brown hues (Wehlte 1967, 114).

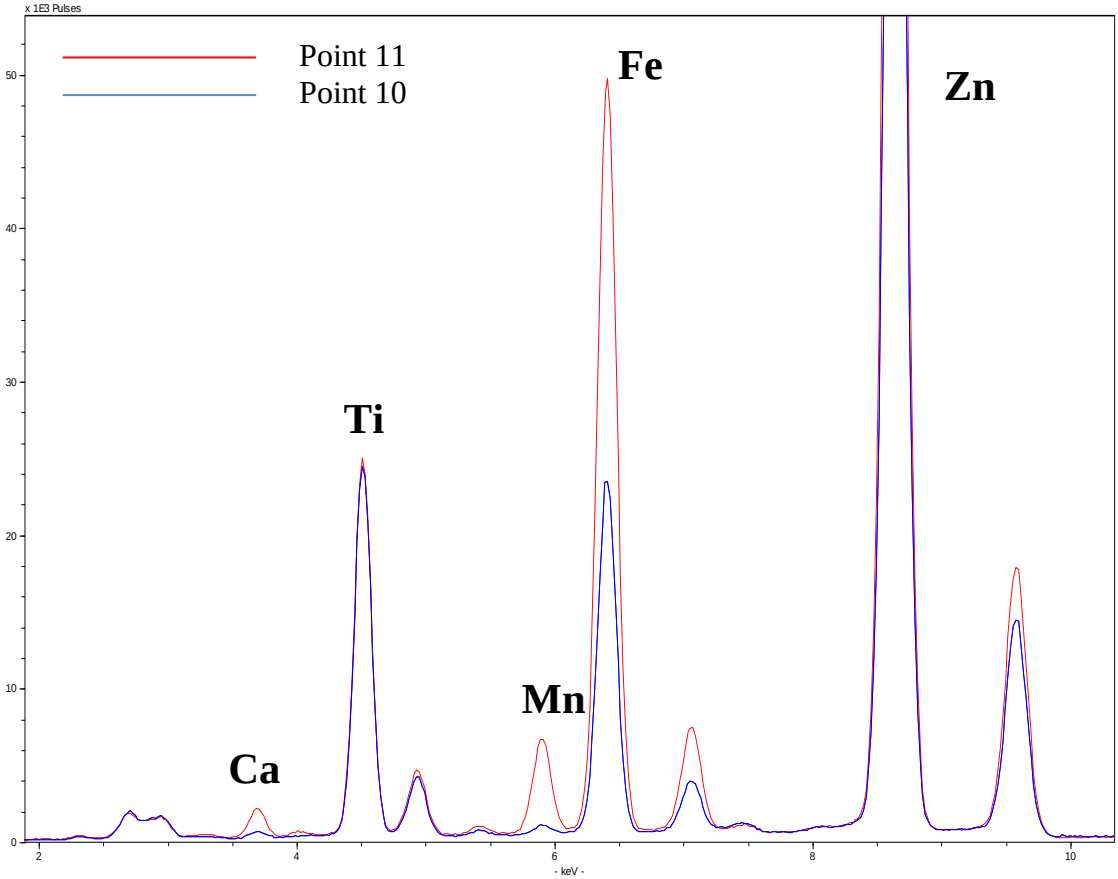

Figure 150. *Bluebonnets in San Antonio*. Point 10, yellow, compared to point 11, brown.

Signature

The signature, as expected, is very similar to the brown. The differences, less iron and manganese, are likely influenced by the information collected on the background below the signature (figure 151). It seems likely that this painting was indeed signed by the same person who painted it, though given the heavy reliance of titanium based white, it seems unlikely that it was actually Julian Onderdonk.

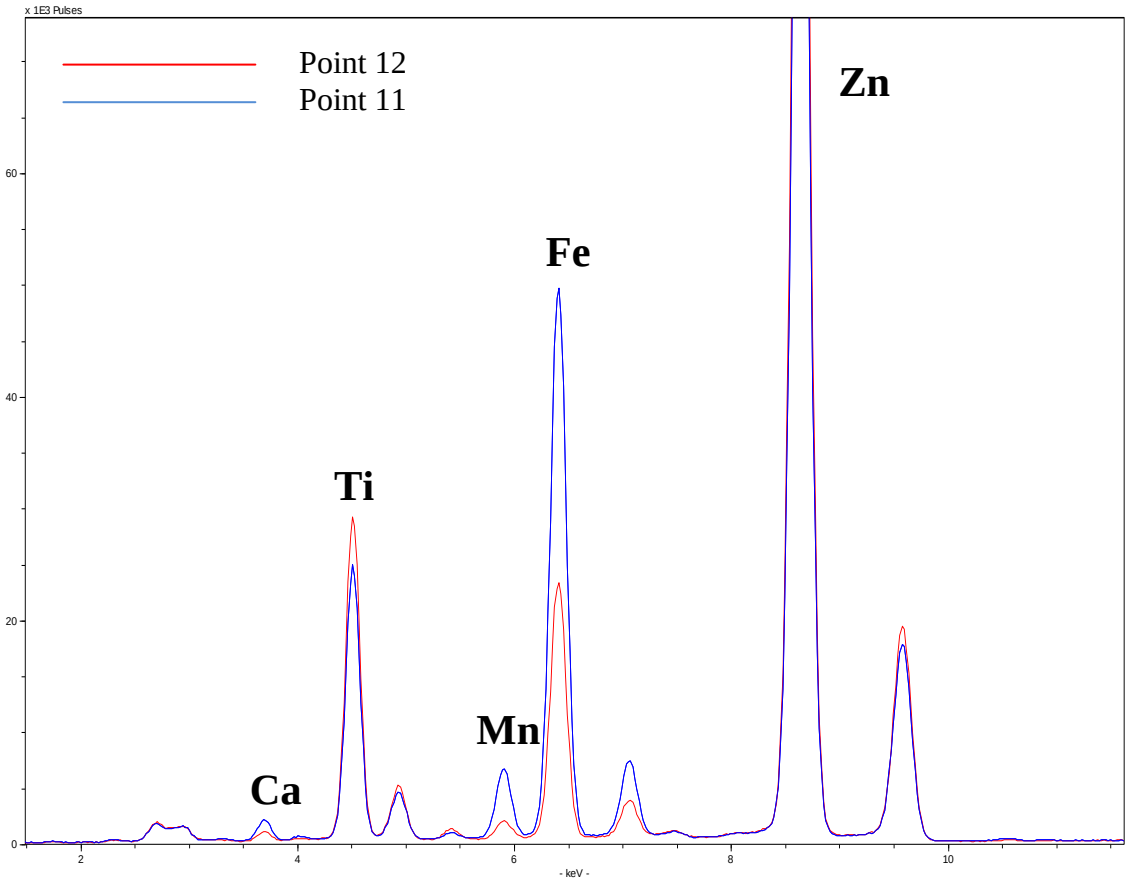

Figure 151. *Bluebonnets in San Antonio*. Point 11, brown, compared to point 12, the signature.

Central Park

Figure 152. *Central Park*, No Date, Signed Julian Onderdonk, Oil on Burlap, 16in x 22in, James and Kimel Baker Collection, College Station, TX. Photo courtesy of James Baker.

A total of ten points were shot for *Central Park* (figure 152). This is a less chromatically varied painting than many of the others, and the consistency across the spectra represent this nicely. Points 1 and 4 are brown, points 2, 3, 8, and 9 are green, point 5 and 7 are a light gray, point 6 is the reddish leaves on the left of the painting, and point 10 is the signature, which is quite dark and was likely painted with black paint.

Brown

The brown of the tree, point 4, is significantly darker than the brown of the dirt, point 1. Point 4 is extremely high in iron compared to point 1, so it is likely that the iron is the darkening agent (figure 153). This could be a variety of pigments, but given the shade, it is likely a red or a green. Given the spectra, the green is most likely viridian, or chromium oxide, and the red is iron based, either hematite or ochre. Comparing point 4 to the signature, point 10, which is situated atop the lighter brown background of point 1 indicates that the iron is indeed the most likely darkening agent, as the iron content for the signature falls approximately halfway between the peak for the lighter point 1 and the darker point 4. The spectra for all three browns exhibit cadmium as well, so it is likely that the lightening agent for the brown is cadmium yellow (CdS), which was available synthetically as far back as 1817, though rare until the 1840s (Artioli 2010, 268).

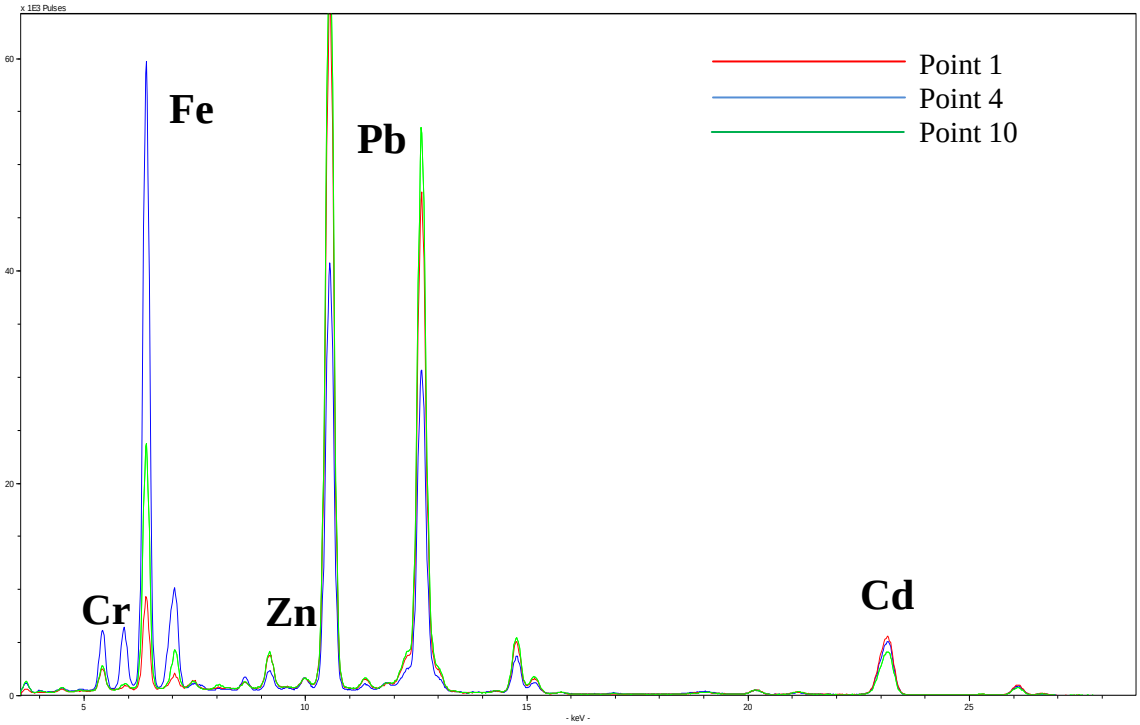

Figure 153. *Central Park*. Points 1 and 10, browns, compared to point 4, the signature.

Green

Points 2, 3, 8, and 9 are all green, but they are very different hues. Each one has a strong chrome component, and spectra for points 2 and 9, the 2 closest to darker colors, have a stronger iron signature (figure 154). As stated above, the most likely green pigment is chromium oxide (Cr_2O_3). No copper signature is present, which rules out the majority of green pigments, leaving only iron based greens, which although possible, would not account for the presence of chromium.

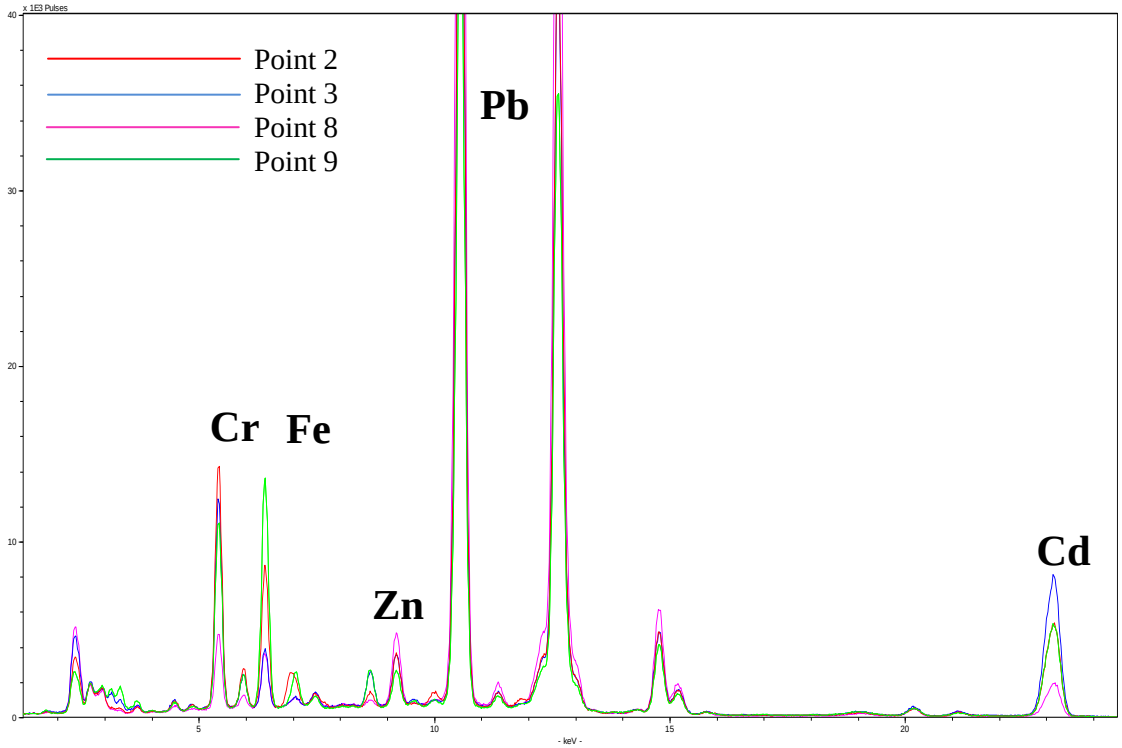

Figure 154. *Central Park*. Points 2, 3, 8, and 9, greens.

Gray / White

There are no pure white areas on the painting, so the best choice for determining the composition of the white paint was the gray from the clouded areas, points 5 and 7. Both are nearly identical, with the exception of point 7 being higher in cadmium and tin (figure 155). Because point 5 is the whiter of the two, it is likely that the spectra for cadmium and tin are the result of other pigments. The white used is a lead-based white.

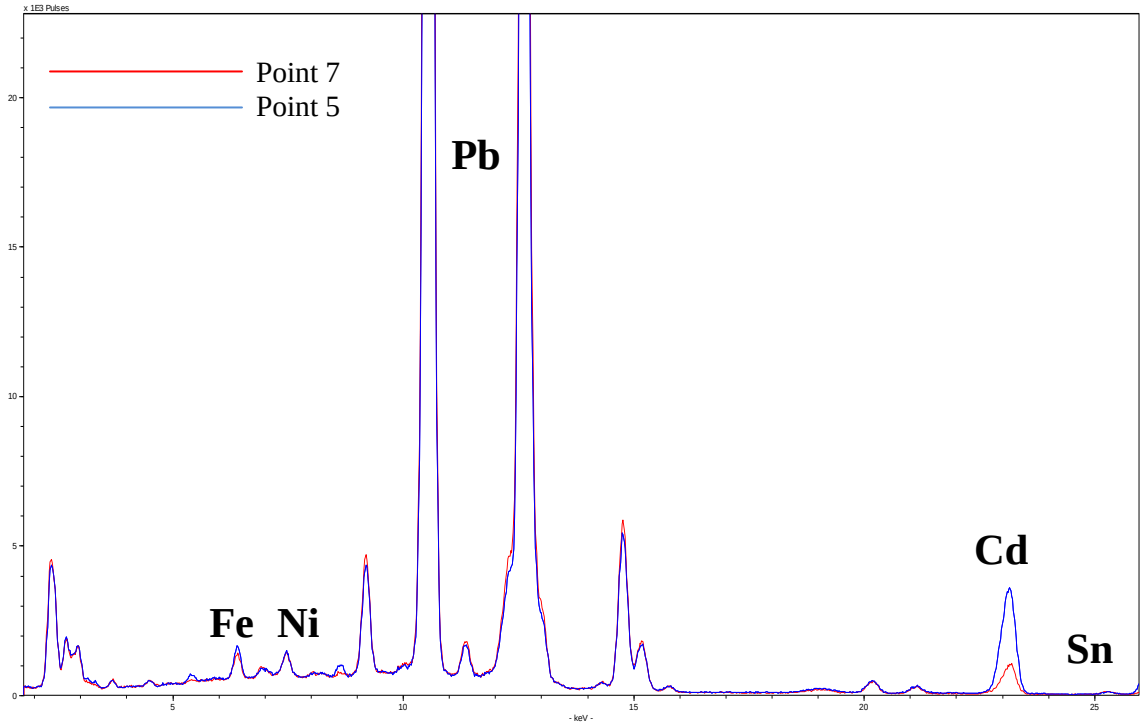

Figure 155. *Central Park.* Points 5 and 7, white.

Red

The best red sample on this painting is from the leaves on the tree on the left of the painting. As previously mentioned, the iron signal in these spectra likely points to hematite. The higher lead content of the gray color indicates that the white is lead based, and though it is possible that the red is lead based, it would not account for the iron (figure 156).

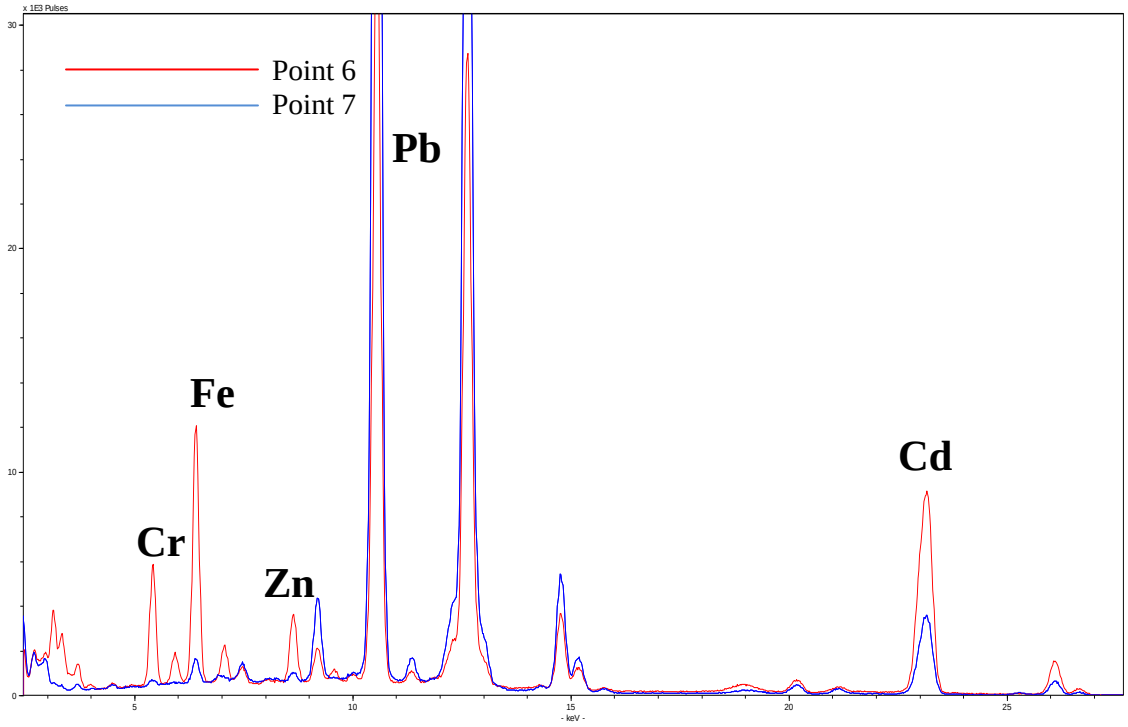

Figure 156. *Central Park*. Points 6, red, compared to point 7, white.

Fall Landscape #2

Figure 157. *Fall Landscape #2*, No Date, Signed Julian Onderdonk, Oil on Board, 10in x 14in, James and Kimel Baker Collection, College Station, TX.

A total of seven points were analyzed for *Fall Landscape #2* (figure 157), which is signed by Julian Onderdonk. Points 1 and 2 are the whites of the clouds, point 3 is the yellow on the top of the trees in the center of the painting, point 4 is green taken from the base of the trees on the left of the painting, point 5 is the red in the trees to the right, point 6 is the blue of the water, and point 7 is the signature.

White

Points 1 and 2 are composed of primarily of lead, with strong indications of barium, zinc, and strontium (figure 158). Lead and barium are both used for white ($Pb_3(CO_3)_2(OH)_2$) and ($BaSO_4$), but it is more likely that the barium and the strontium are from the yellowish tint to the cloud, indicating lemon yellow, which can be made with either barium ($BaCrO_4$) or strontium ($SrCrO_4$).

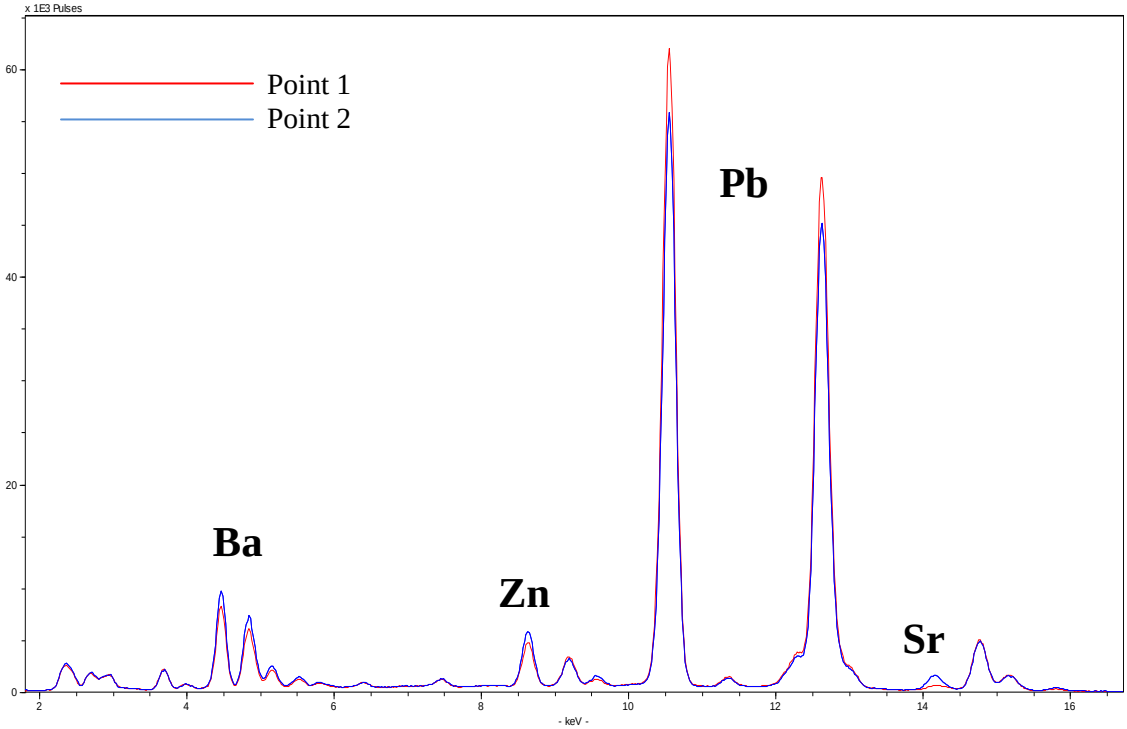

Figure 158. *Fall Landscape #2*. Points 1 and 2, whites.

Yellow

As mentioned above, point 3, the yellow taken from the top of the tree has barium and strontium, and is likely lemon yellow. There are significant levels of zinc, which is also seen in the white of points 1 and 2, chromium, which is from the lemon yellow, and mercury, from the red (figure 159).

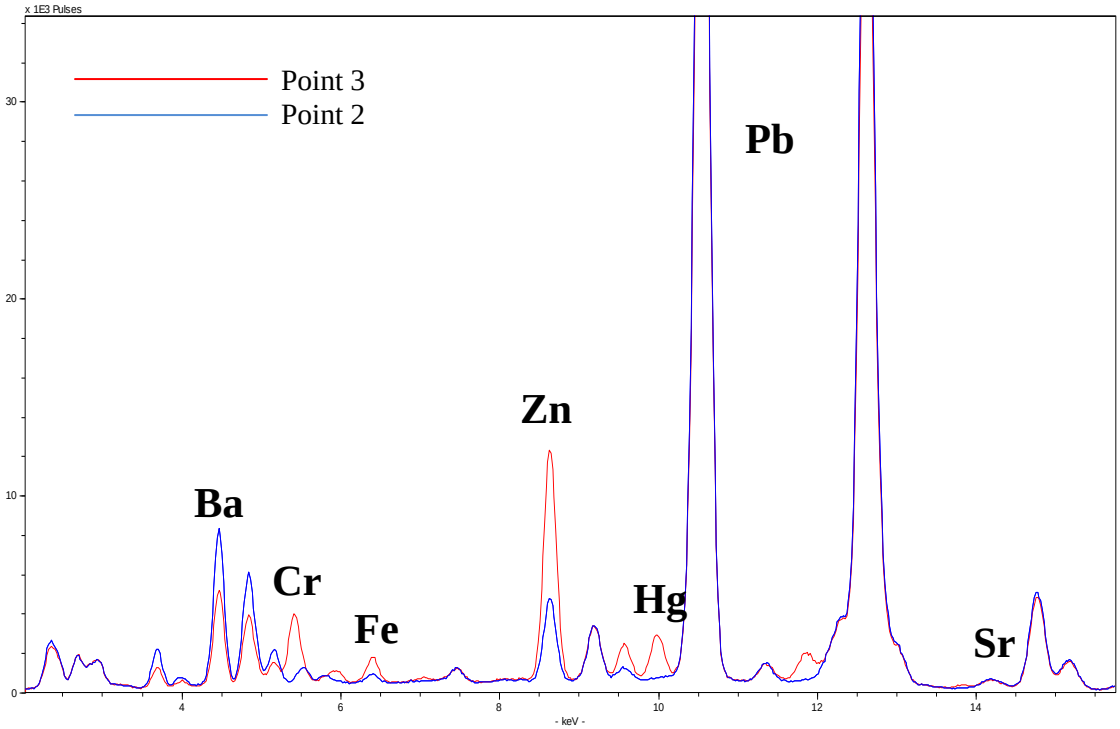

Figure 159. *Fall Landscape #2*. Point 3, yellow, compared to point 2, white.

Green

Point 4 is green, taken from the base of the trees on the left of the painting. The spectra for the green, obviously mixed with some of the other colors, has a higher signal from chromium than the others, likely pointing to viridian green, a chromium oxide dehydrate ($Cr_2O_3 \cdot 2\ H_2O$). The high level of zinc visible was also seen in the yellow, and therefore it is most likely from this pigment (figure 160).

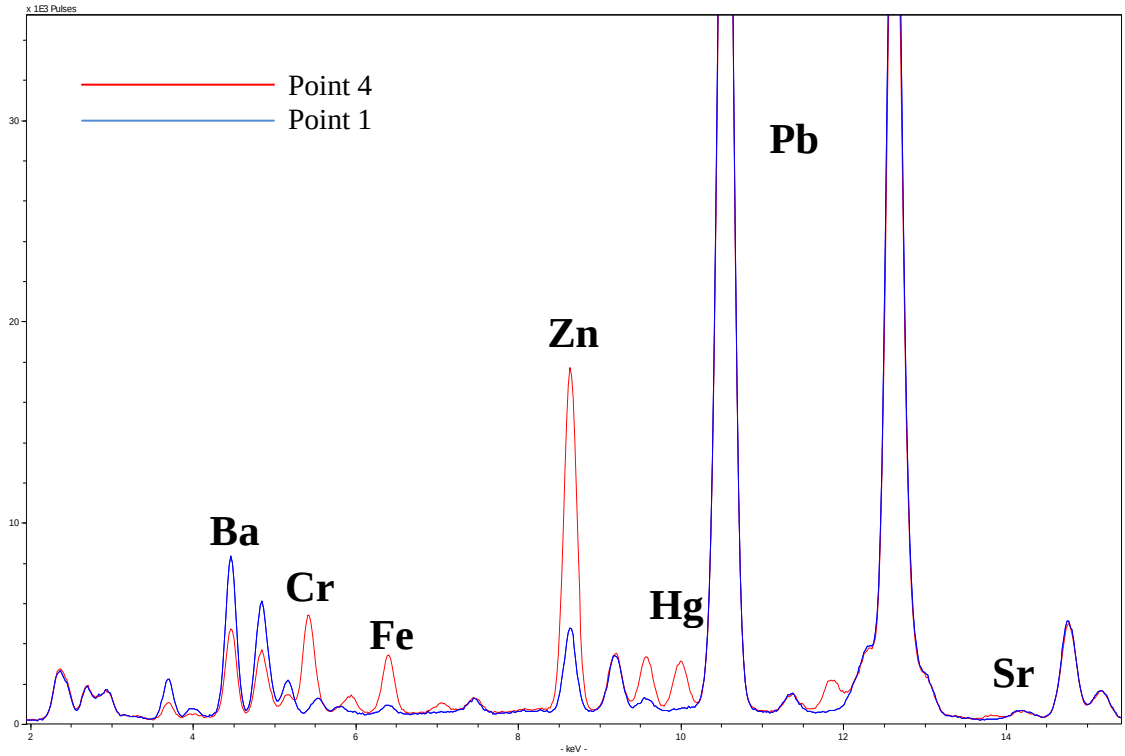

Figure 160. *Fall Landscape #2*. Point 4, green, compared to point 1, white.

Red

Point 5, the red, taken from the top of the tree to the right of the painting, is dominated by the spectra for mercury, pointing to realgar as a pigment (figure 161). Compared to yellow point 3, the mercury content is higher, which points to the red as being most likely the origin of the mercury in the yellow.

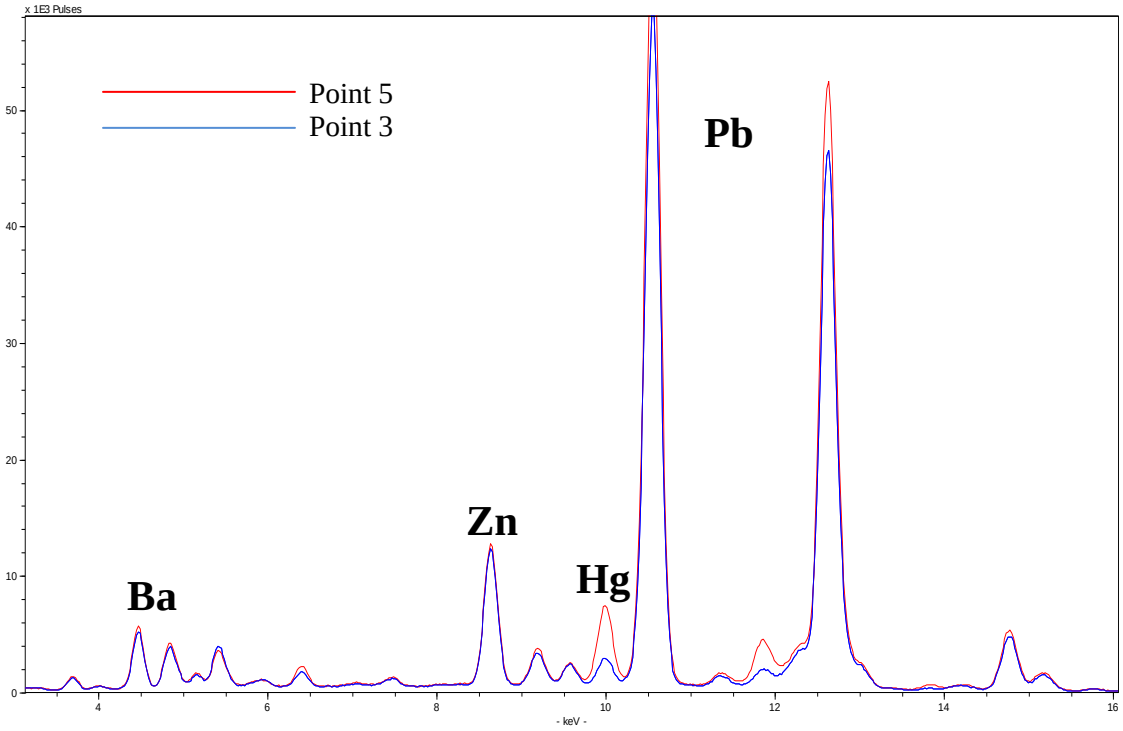

Figure 161. *Fall Landscape #2*. Point 5, red, compared to point 3, yellow.

Blue

Point 6 is the blue of the river at the bottom center of the painting. It is apparent that the blue is mixed with some white, so the clearest way to determine the elemental makeup of the blue pigment is to compare it with the white. When overlaid, the spectral energy is higher for zinc, iron, and copper in the blue (figure 162). Given that the copper does not show up in any of the other pigments, the blue is very likely to be a copper based blue pigment. There are several possibilities, including azurite $Cu(CO_3)_2(OH)_2$, Egyptian blue ($CaCuSi4O_{10}$), or Han blue ($BaCuSi_2O_6$), but without knowing the chemical structure or the organic compounds present, it is impossible to isolate just one. If the barium is indeed from the yellow, then this might point to Han blue, but if it is from the white, then any of them are possible. Given the elevated iron, it is also possible that Prussian blue ($Fe_4[Fe(CN)_6]_3$) was used, though the iron could be from black magnetite.

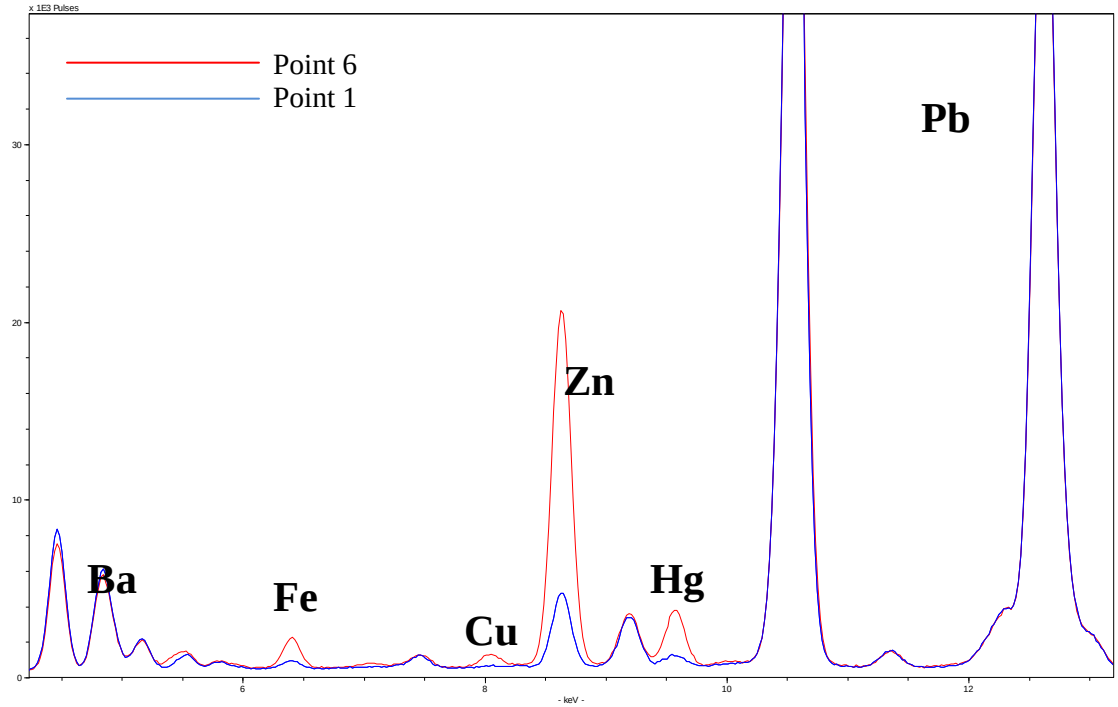

Figure 162. *Fall Landscape #2*. Point 6, blue, compared to point 1, white.

Signature

Point 7, the signature in the bottom left of the painting is very similar to point 4, the green it is painted atop. There are slightly higher levels of mercury (red), chromium (green), and iron (either black, blue, green, yellow or red), and a slightly lower level of barium (yellow) (figure 163). It is likely that the dark brown of the signature is the result of a blending of several of the paints. What is important about the signature is that the spectral profile is consistent across the painting, which points towards a consistent painter.

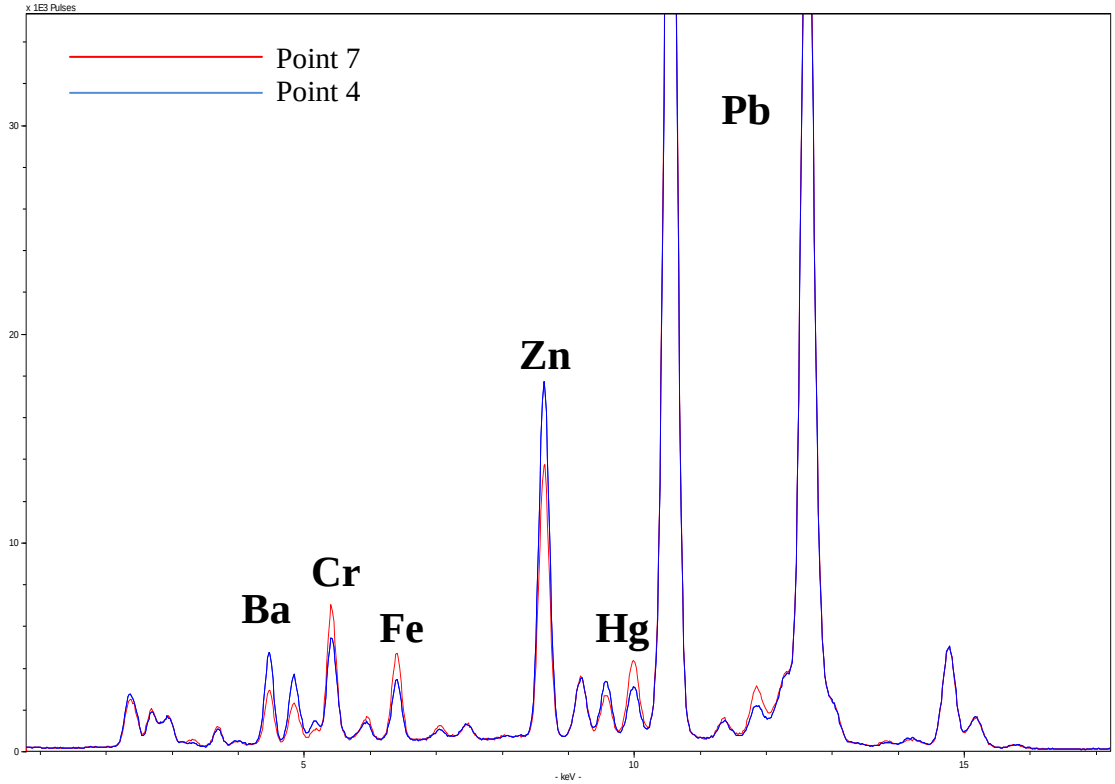

Figure 163. *Fall Landscape #2*. Point 7, the signature, compared to point 4, the green.

Large Bluebonnet Landscape

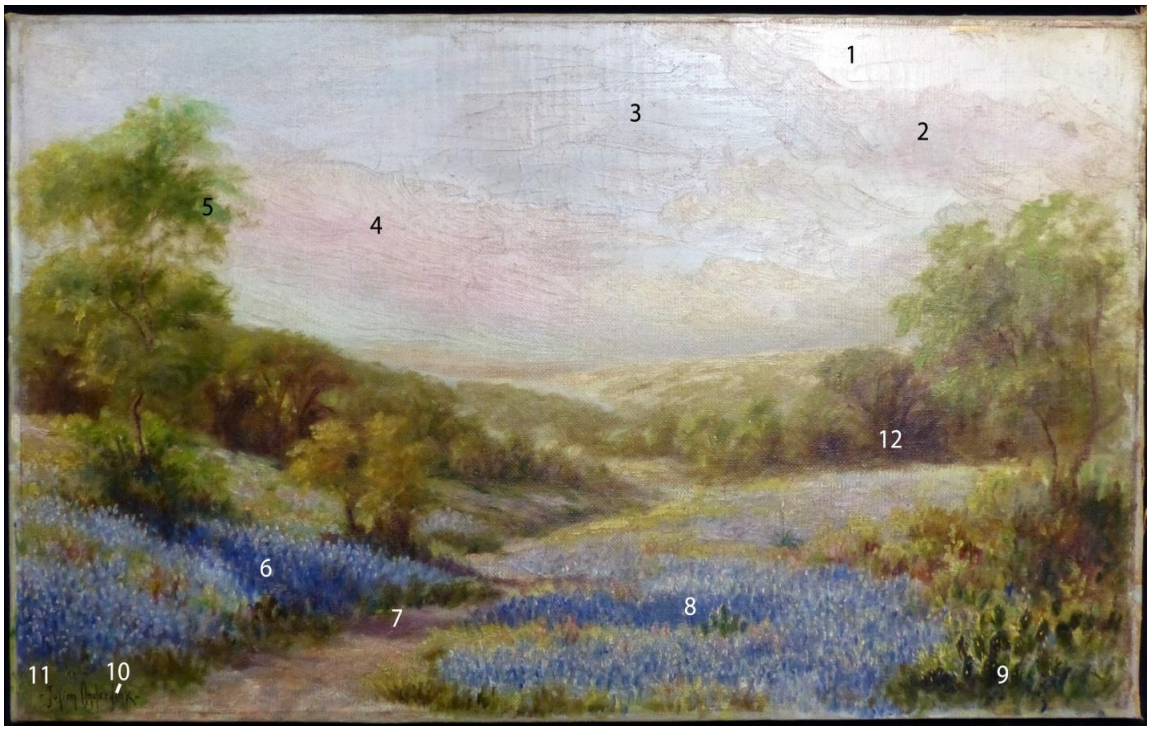

Figure 164. *Large Bluebonnet Landscape*. No Date, Signed Julian Onderdonk, Oil on Canvas, 16in x 28in, James and Kimel Baker Collection, College Station, TX.

For *Large Bluebonnet Landscape* (figure 164), thirteen points were taken. Point 1 is the brightest white in the sky, while points 2, 3, and 4 are other shades taken from the sky. Point 5 is the green of the tree to the left, points 6 and 8 are the blue of the flowers, point 7 is the purple in the path, point 9 and 11 are dark greens in the foreground, point 10 is the signature 'Julian Onderdonk', point 12 is the brown of the tree to the right, and point 13 was taken on the primer on the bottom side of the canvas.

White

As seen in figure 165, the white used in point 1 is zinc white (ZnO).

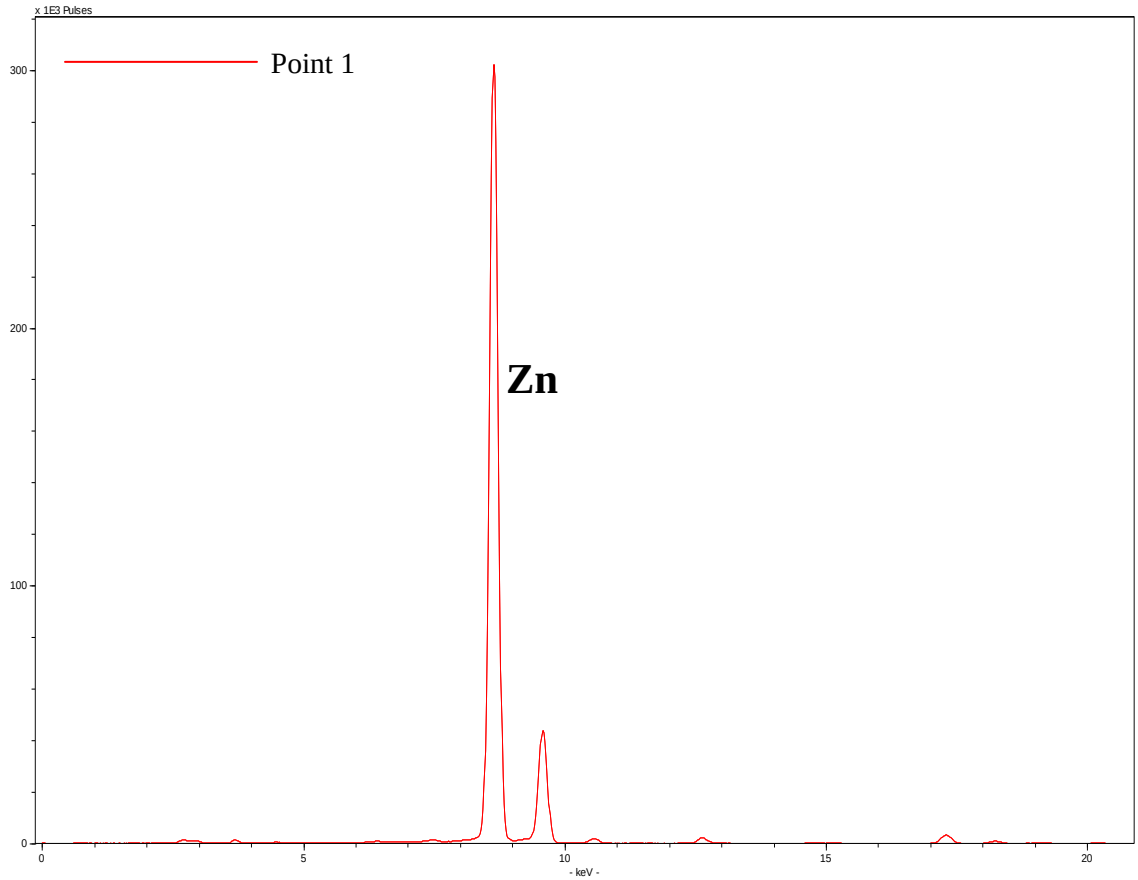

Figure 165. *Large Bluebonnet Landscape*. Point 1, zinc white.

Red/Gray

Points 2, 3, and 4 are similar in color, all three having blue and red in them. Point 3 has less red, and spectrally it is much more similar to the reddest point, point 4, than it is to point 2. Point 2 is unusual in that it exhibits a much stronger signal for iron, and a significant signal for calcium and titanium (figure 166). This is the only point analyzed that contained titanium, and based on black light analysis of the painting, the titanium point is an area that has been repaired by restoration efforts (figure 167). For all 3 points, the presence of lead and iron likely indicate ochre and red lead.

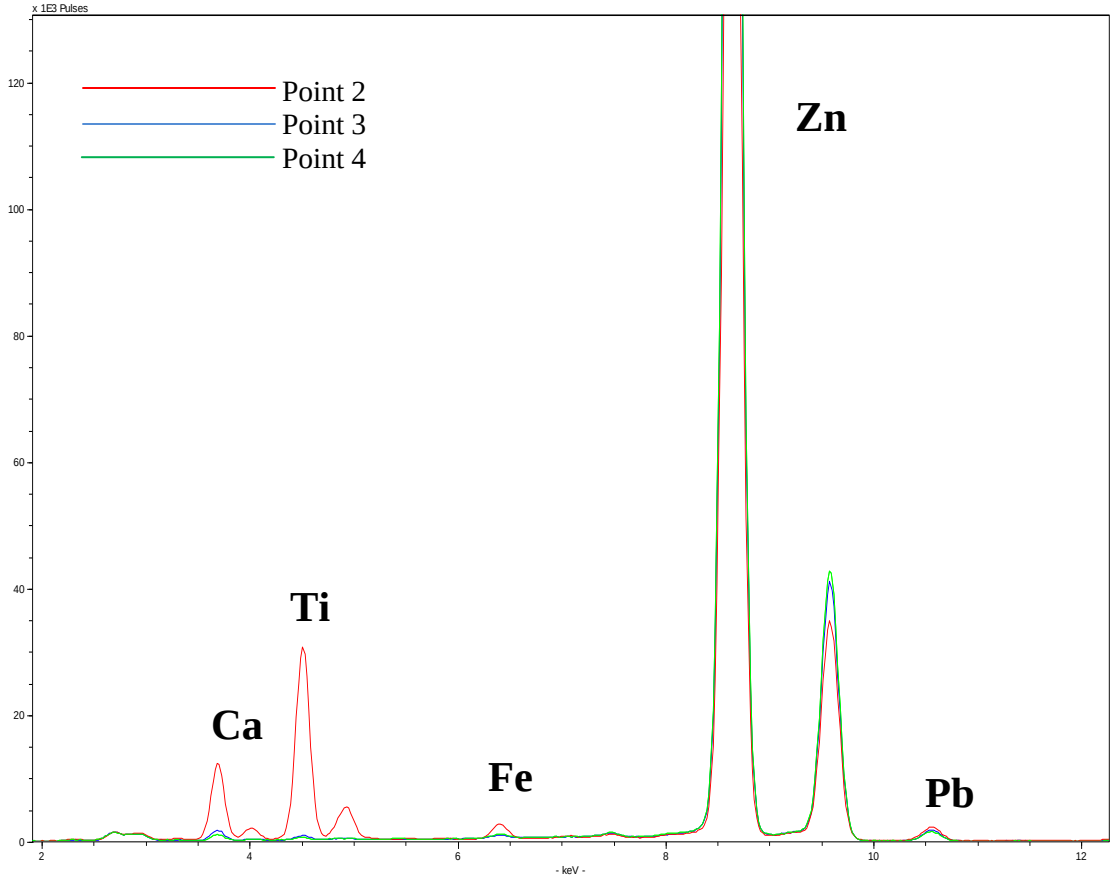

Figure 166. *Large Bluebonnet Landscape*. Points 2, 3, and 4, red and gray.

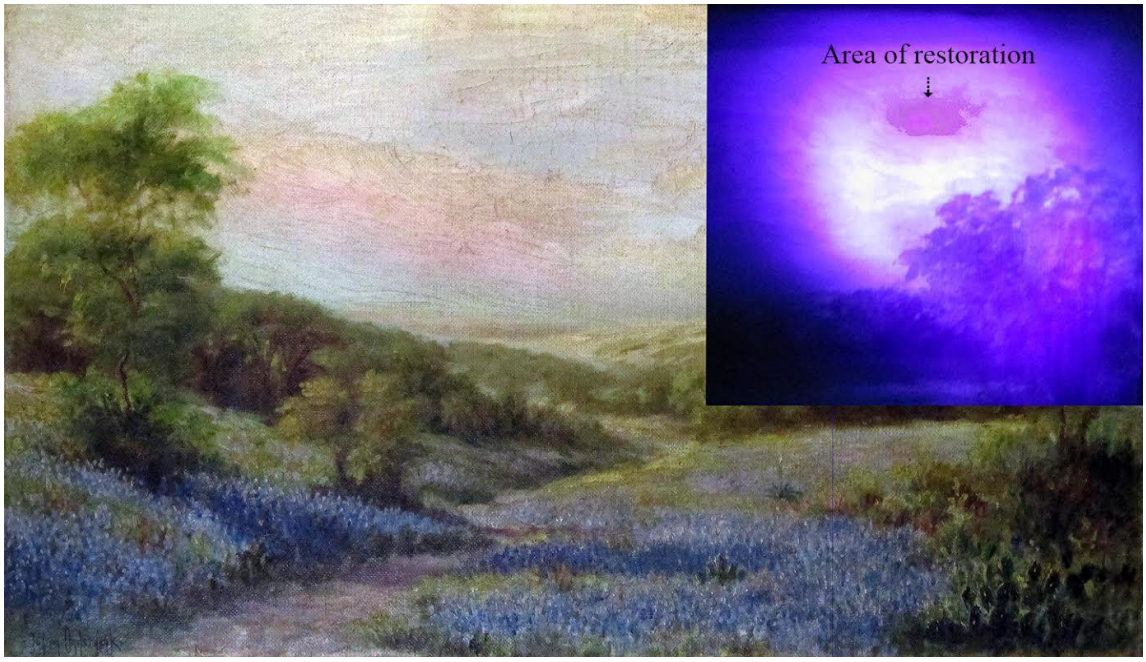

Figure 167. *Large Bluebonnet Landscape*. Black light analysis showing the area of restoration where the titanium white peak was observed in point 2. Picture courtesy of James Baker.

Blue

Points 6 and 8 are the blues of the bluebells. Both spectra are dominated by zinc, but compared to the white of point 1 they have high levels of barium, chromium, iron, cobalt, copper, and arsenic (figure 168). The barium combined with the copper indicates the use of Han blue ($BaCuSi_2O_6$), while the chromium and the cobalt indicates the use of azurite ($Cu_3(Co_3)_2(OH)_2$. The iron could represent Prussian blue, but given that there are already two (or more) blue pigments being used, it is also possible that the iron represents the red mentioned above. Interestingly, point 3, the bluest part of the sky, exhibits comparatively low energy from chromium, cobalt, copper, and strontium. This might indicate that an organic blue pigment was also used, such as indigo.

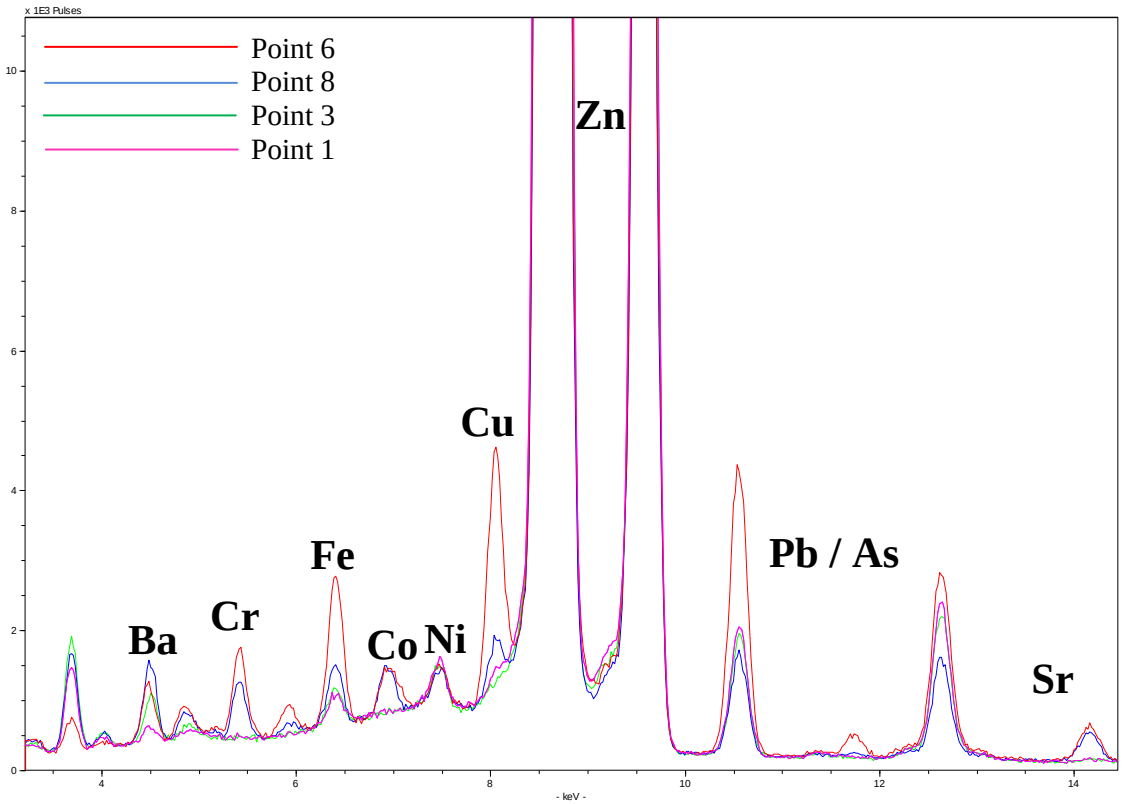

Figure 168. *Large Bluebonnet Landscape*. Points 6 and 8, blue, compared to point 3, blue, and 1, white.

Purple

The purple of the path between the two patches of bluebonnets, point 7, can be explained in two distinct and equally plausible ways. Because of the presence of cobalt and arsenic (figure 169), it could be cobalt violet ($Co_3(AsO_4)$), which was introduced in 1859 and would have been available to Onderdonk (Wehlte 1975, 157). However, cobalt violet was expensive and weak, and was therefore not very popular among painters. The other possible explanation for the purple is a blending of red and blue, which, if true, is helpful in understanding the red in point 4 and the blues of points 6 and 8 more clearly. When comparing the three spectra, point 6, the blue, has the highest level of cobalt, copper, and iron, which holds well with what was suggested above. The light grayish red/pink from point 4 has the highest level of calcium and zinc, which, since there is no presence of copper signifying the calcium is from Egyptian blue, suggests that both are strong signals from the white. The purple, not being drowned out by the strength of the zinc in the white, is highest in Arsenic and lead, suggesting that the red is realgar (As_4S_4) and red lead (PbO or Pb_3O_4).

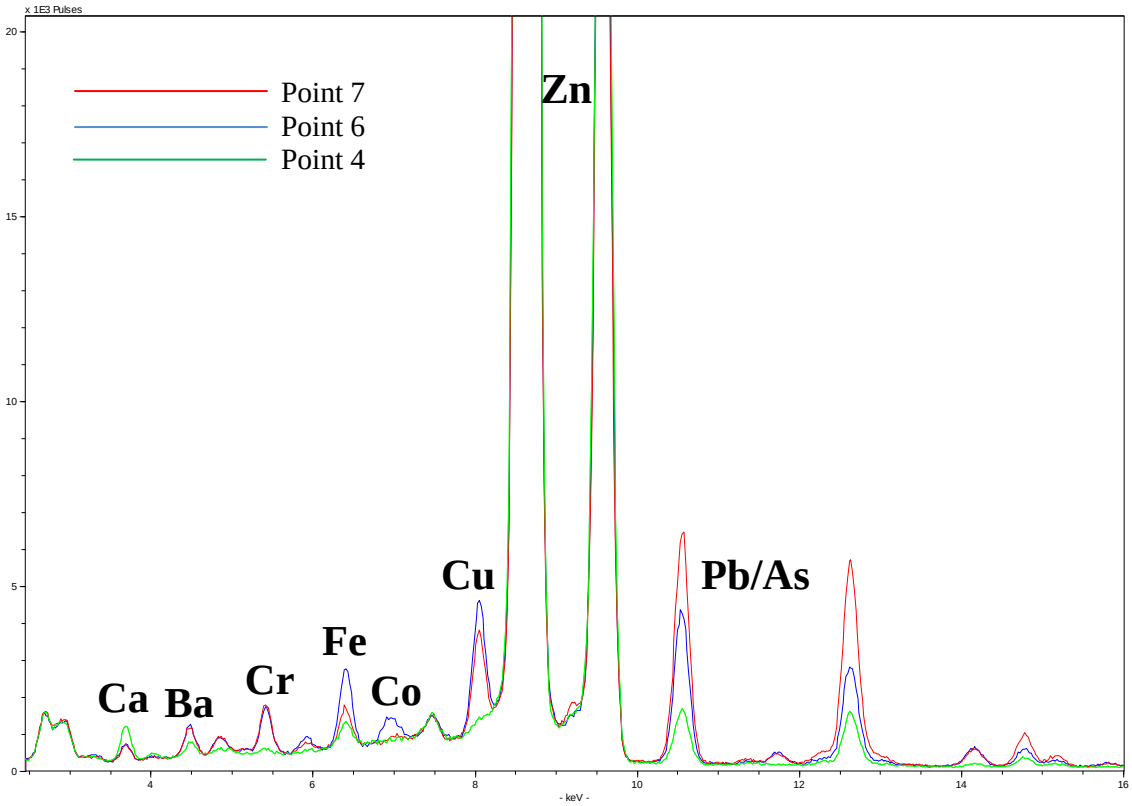

Figure 169. *Large Bluebonnet Landscape*. Point 7, violet, compared to point 6, blue, and point 4, red.

Green and Yellow

Points 5, 9, and 11 are all green, though each is obviously influenced by the paints below them. Point 5 is a light green painting atop the sky, and not surprisingly has the strongest zinc signal associated with white (figure 170). Point 9 is the dark green mixed with brown on the right side of the painting, and had the strongest chromium and lead signal, associated with red. Point 11, the green of the grass on the bottom left of the painting has the highest iron, copper, and strontium. All three have chromium, strontium, copper, lead, arsenic, and zinc. The green is likely two pigments, viridian (from cobalt) and one of the many copper sources of green, such as atacamite, chrysocolla, malachite, verdigris, or Egyptian green. Even without a pure yellow point, the presence of strontium and chromium in the green infers that that the yellow is lemon yellow.

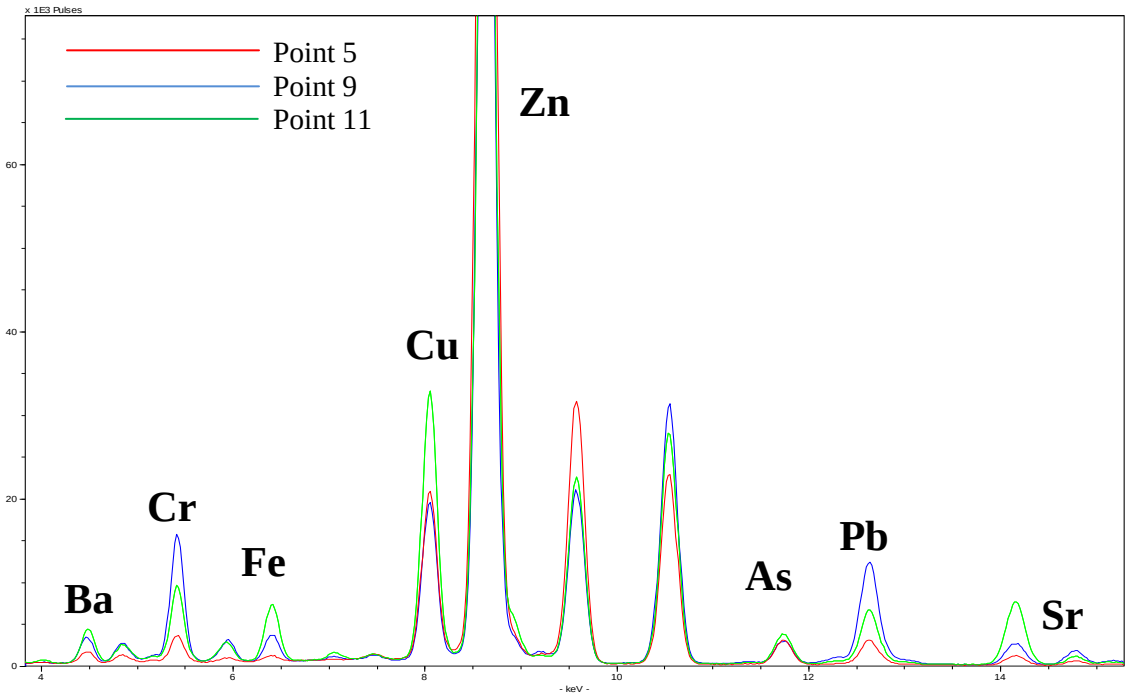

Figure 170. *Large Bluebonnet Landscape*. Point 7, violet, compared to point 6, blue, and point 4, red.

Brown

Point 12, the brown of the tree trunk on the right of the picture, appears to be a strong representative of red, green and yellow. The chromium is higher in point 12 than any of the other spectra, which would be expected if it were coming from both green and yellow pigments. The arsenic and lead of the red both have a strong signal, and the copper of the green, and the strontium of the yellow have distinct peaks. When compared to the spectra of point 5 and point 7, point 12 serves as a logical validation of the claims made about all three of these pigments (figure 171).

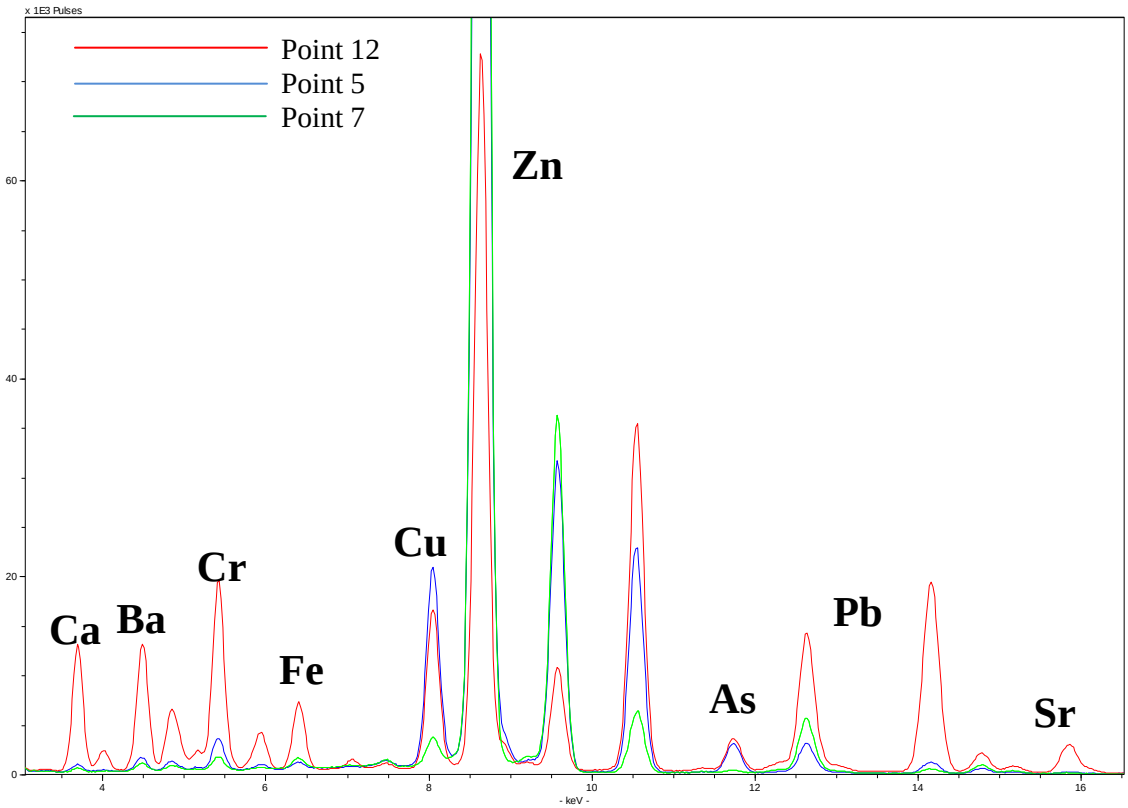

Figure 171. *Large Bluebonnet Landscape*. Point 12, brown, compared with point 5, green, and point 7, violet.

Signature

Comparing point 10, the signature, to point 11, the area just adjacent to it makes it fairly easy to discern what elements are in the signature ink and not coming from the background. Calcium, barium, and lead are the only signals stronger in the signature than the background (figure 172). The high level of calcium indicates the presence of an organic black, mixed with red lead and lemon yellow.

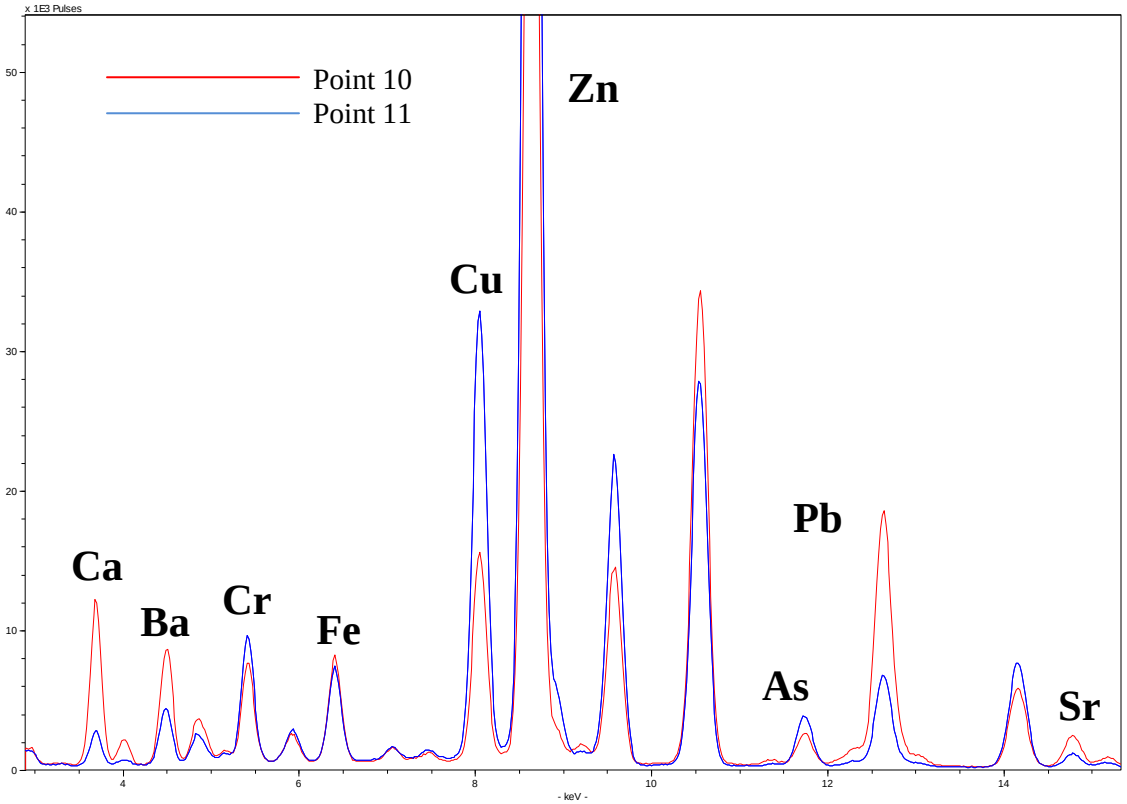

Figure 172. *Large Bluebonnet Landscape*. Point 11, the signature, compared to point 12, the green around it.

Primer

The primer is, unlike the rest of the painting, overwhelmingly lead white (figure 173). There are also strong signals for barium, zinc, and small signals for iron, zinc, and strontium.The zinc peak could be zinc white, and the barium peak might indicate the use of *Blanc fixe*, a barium sulfate white introduced around 1830 that is known to be a particularly brilliant white (Wehlte 1967, 69). For this particular painting, the primer layer is very dissimilar to the paints atop it.

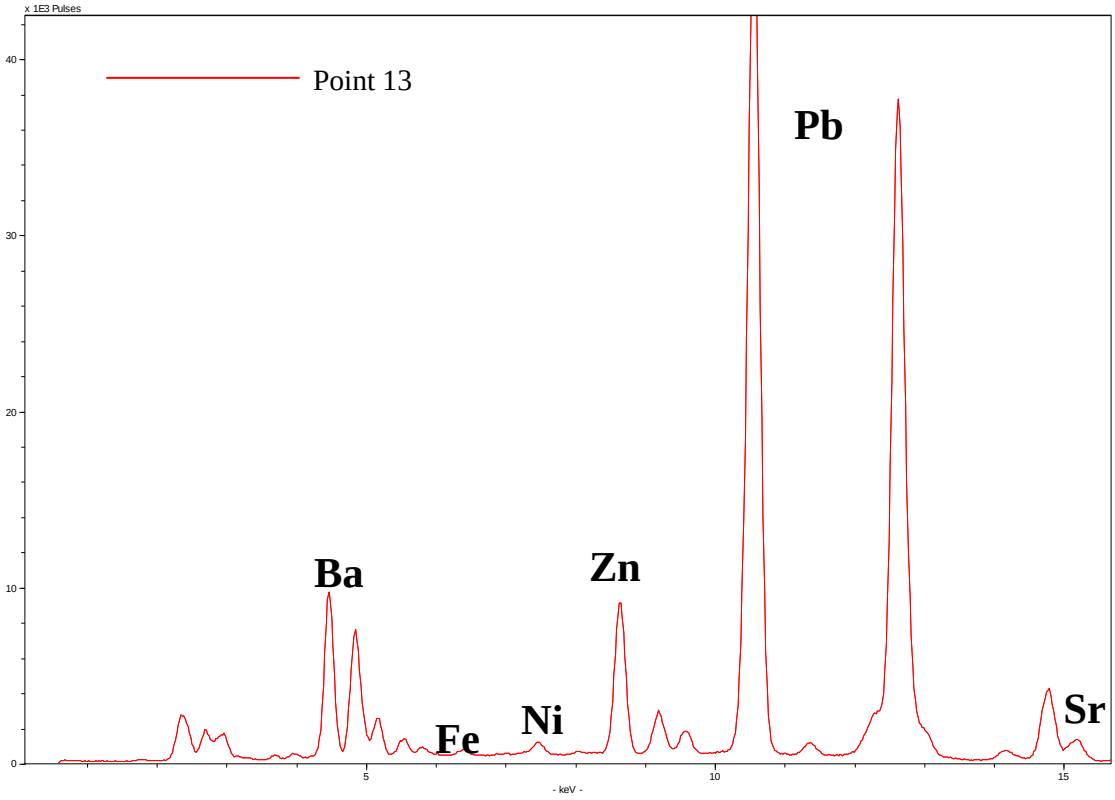

Figure 173. *Large Bluebonnet Landscape*. Point 13, primer.

Summer Afternoon

Figure 174. *Summer Afternoon*. No Date, Signed Julian Onderdonk, Oil on Canvas, 13in x 18.675in, James and Kimel Baker Collection, College Station, TX.

For *Summer Afternoon* (figure 174), twelve points were analyzed. Points 1-5 were of the various whites, points 6, 7, and 8 are blues of the sky, 9 and 10 are greens of the grass, and points 11 and 12 are browns.

Whites

The white in the clouds of points 1 and 2 have nearly identical lead white spectra. Points 4 and 5, the white structures in the center of the painting, are similar, but contain higher levels of zinc, iron, and chromium. Point 5 additionally has a higher level of barium (figure 175). With the presence of zinc, barium, and chromium, this could indicate the use of zinc yellow or barium yellow ($ZnCrO_4$ and $BaCrO_4$). This is not the case for point 3, the cloud on the upper right of the painting. This point has significantly higher levels of barium and zinc than even point 5, and no chromium. This means instead of zinc and barium yellow, these are zinc and barium whites (ZnO and $BaSO_4$). Unfortunately, this cannot be confirmed without the presence of sulfur, and the *M*-α1 energy from the lead masks the presence of sulfur in this spectra. Even so, it is most likely zinc and barium white.

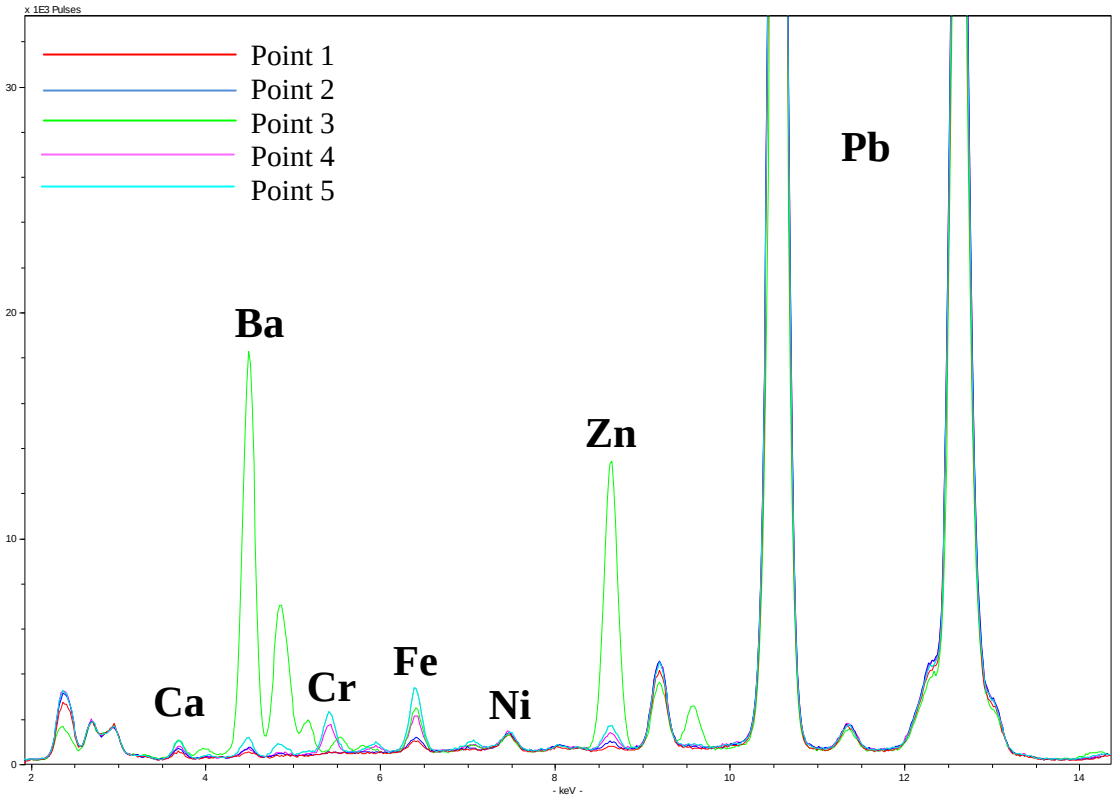

Figure 175. *Summer Afternoon*. Points 1-5, whites.

Blue

The blue points 6 through 8 are, once again, nearly identical to point 1, the lead white (figure 176). This means that the blue is most likely from an organic source that the pXRF is not sensitive to, like indigo blue.

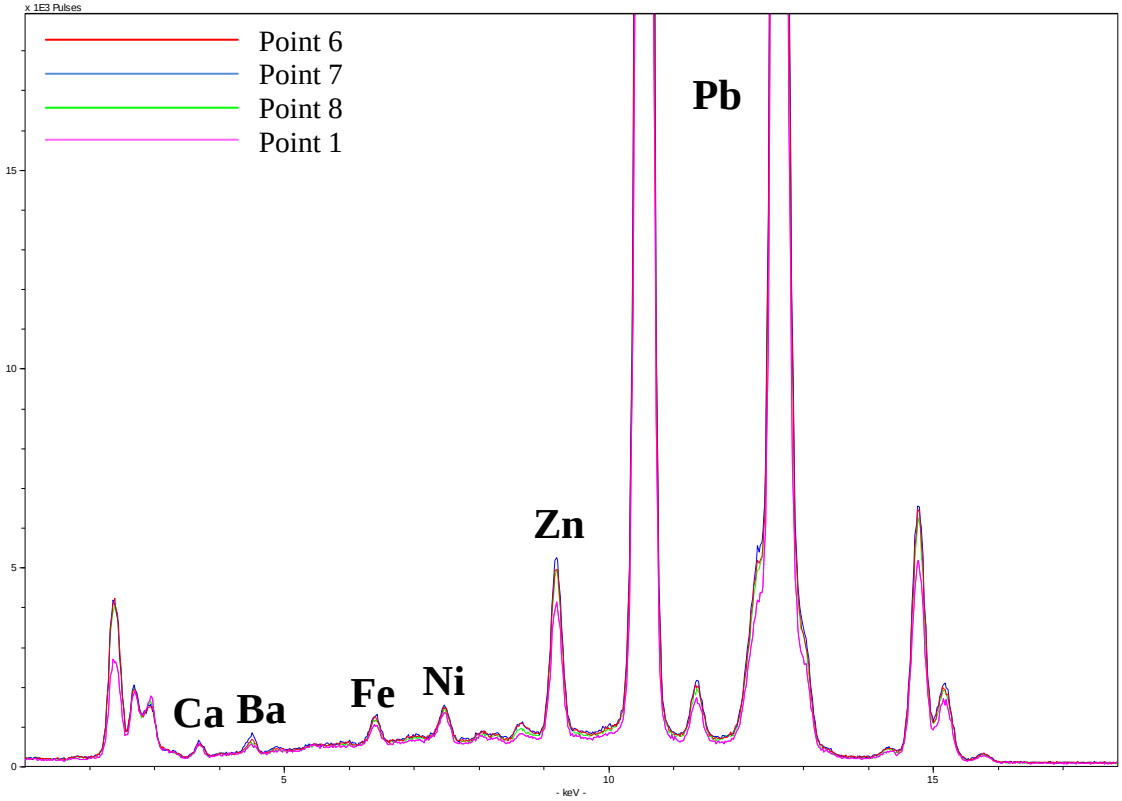

Figure 176. *Summer Afternoon*. Points 6-8, blues, compared to point 1, white.

Green

Points 9 and 10 are green, taken from the grass in the foreground of the painting. Both green contain chromium, which points to chromium green (figure 177). Point 9 has higher iron, while point 10 has much higher zinc. The iron likely represents an ochre, while the zinc could be zinc white or yellow.

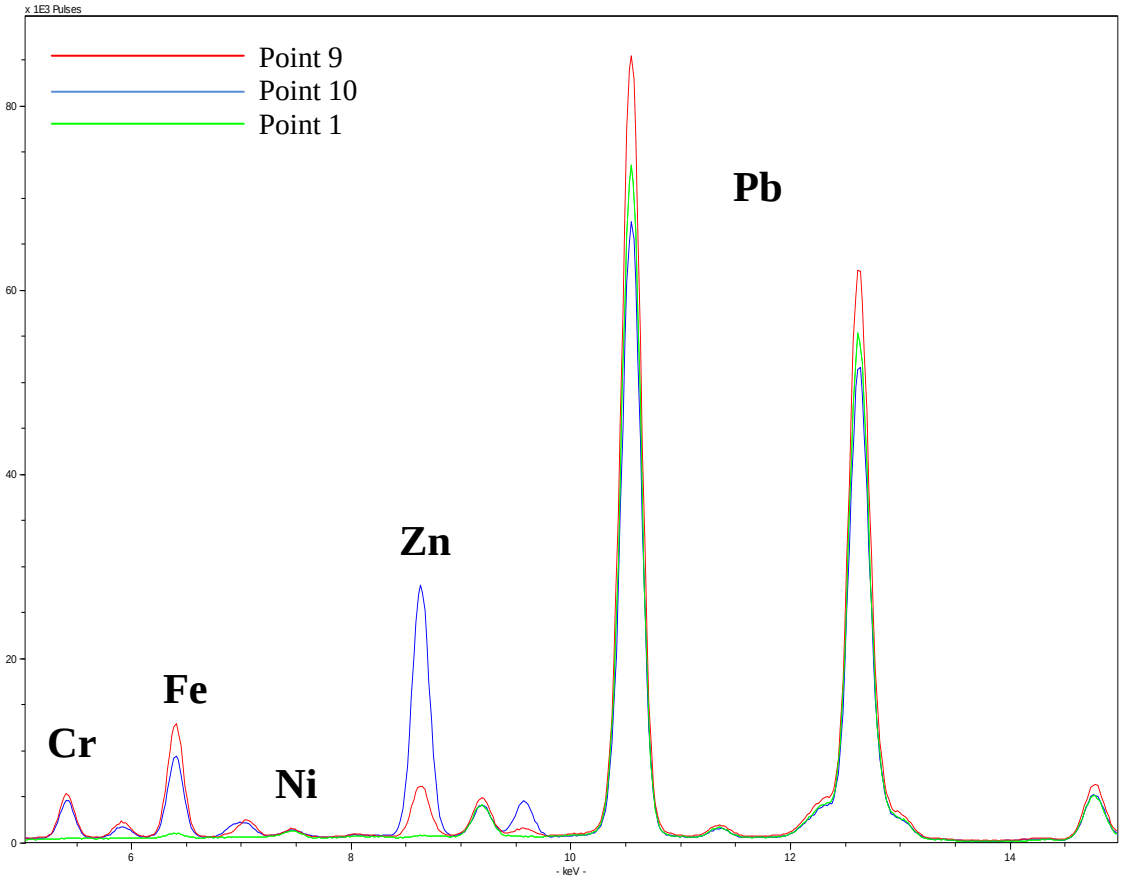

Figure 177. *Summer Afternoon*. Points 9 and 10, greens, compared to point 1, white.

Brown

The browns, points 11 and 12, are characterized by their high levels of iron, manganese, and calcium (figure 178), meaning they are likely an ochre or umber, which have been in use since at least the 17th century, probably before that (Artioli 2010:268). There are also peaks for zinc, barium and chromium, which could be lemon yellow, zinc yellow, or chromium green.

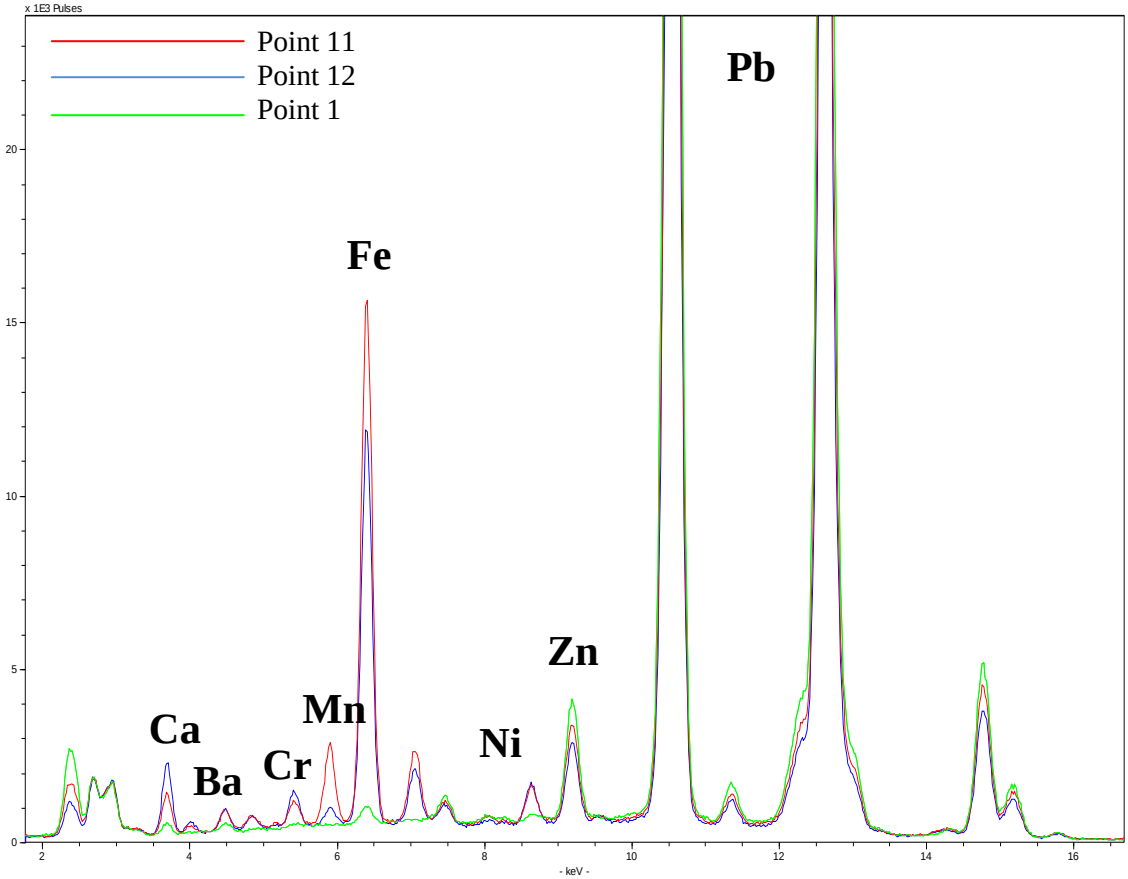

Figure 178. *Summer Afternoon*. Points 11 and 12, browns, compared to point 1, white.

Bluebonnets on a Texas Landscape

Figure 179. *Bluebonnets on a Texas Landscape*. No Date, Signed Julian Onderdonk, Oil on Canvas, James and Kimel Baker Collection, College Station, TX.

For *Bluebonnets on a Texas Landscape* (figure 179), eight points were analyzed. Point 1 is a white highlight on a rock in the field, point 2 is the light green of a bush, point 3 is the brown of a tree trunk, point 4 is the blue of the flowers, point 5 is the brown of the rocks to the left, point 6 is the signature, point 7 is the white of a cloud, and point 8 is the blue of the sky.

White

The white of points 1 and 7 are nearly identical peaks for zinc and lead, indicating zinc white and lead white (figure 180). The consistencies of the height of these two peaks throughout all of the points analyzed on this painting are unique in this study. There is only a slight increase in the height of the zinc peak between the white points and the other colors. This painting was likely painted with a zinc and lead white primer, and the white in the painting appears to have been done with zinc white.

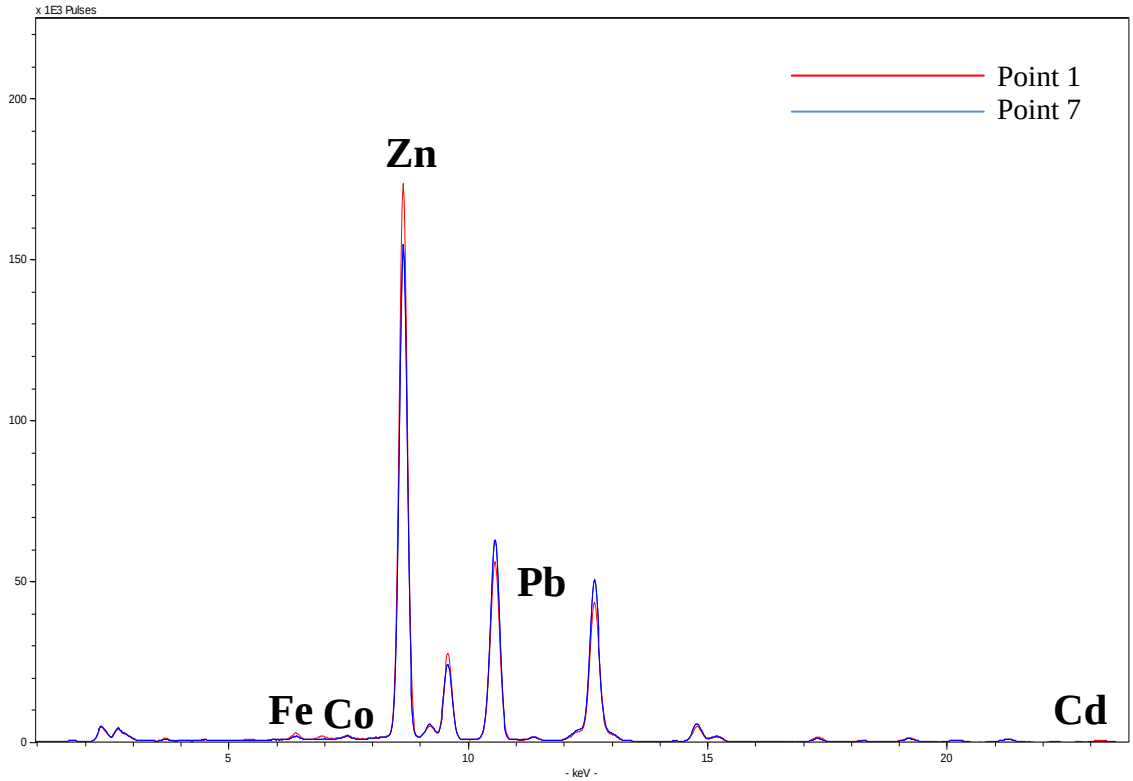

Figure 180. *Bluebonnets on a Texas Landscape.* Points 1 and 7, whites.

Green

Contrasted against the white of point 1, the green appears to be a mix of chromium green and cadmium yellow. The chromium and the zinc could be zinc yellow, but given that the zinc level drops compared to the white point, it is unlikely that more zinc was added to the area over the primer (figure 181). That would suggest that the chromium was chromium oxide, and the presence of cadmium and sulfur would suggest cadmium yellow (CdS).

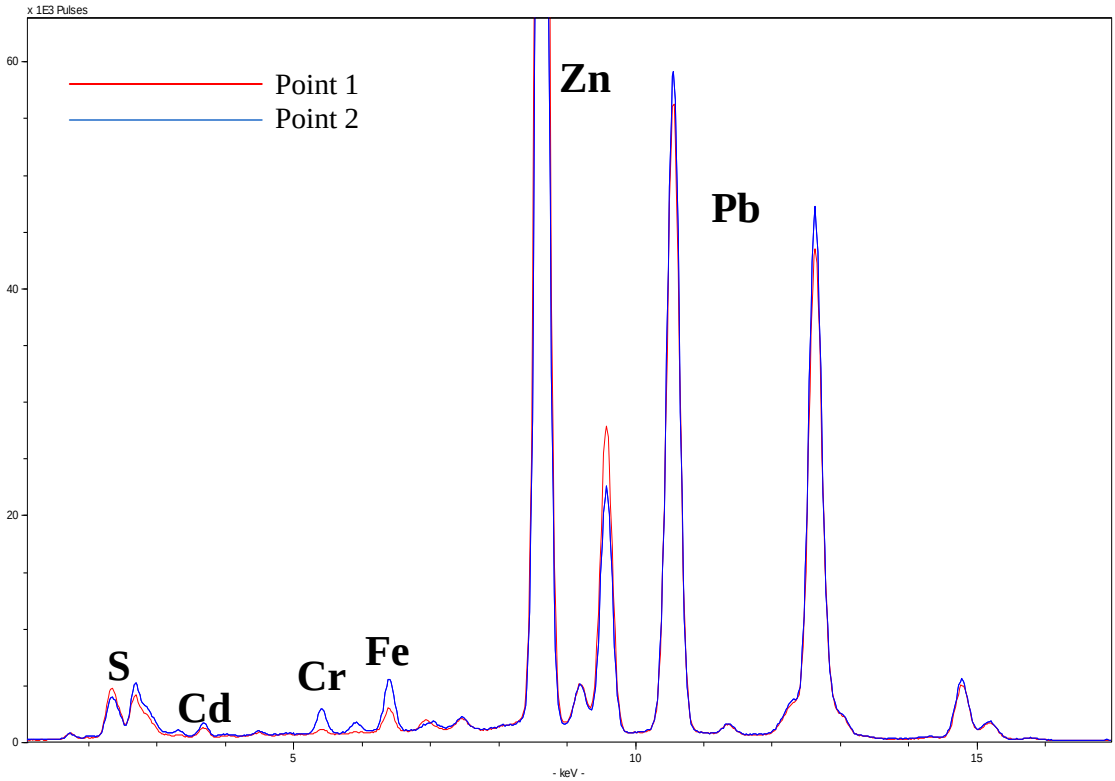

Figure 181. *Bluebonnets on a Texas Landscape*. Points 1, white, compared to point 2, green.

Brown

The tree trunk of point 3, the rock of point 5, and the signature area are all a reddish brown. All three have a distinct iron peaks, suggesting hematite (figure 182). Points 3 and 5, the tree trunk and the brown rock, also have a peak for manganese.

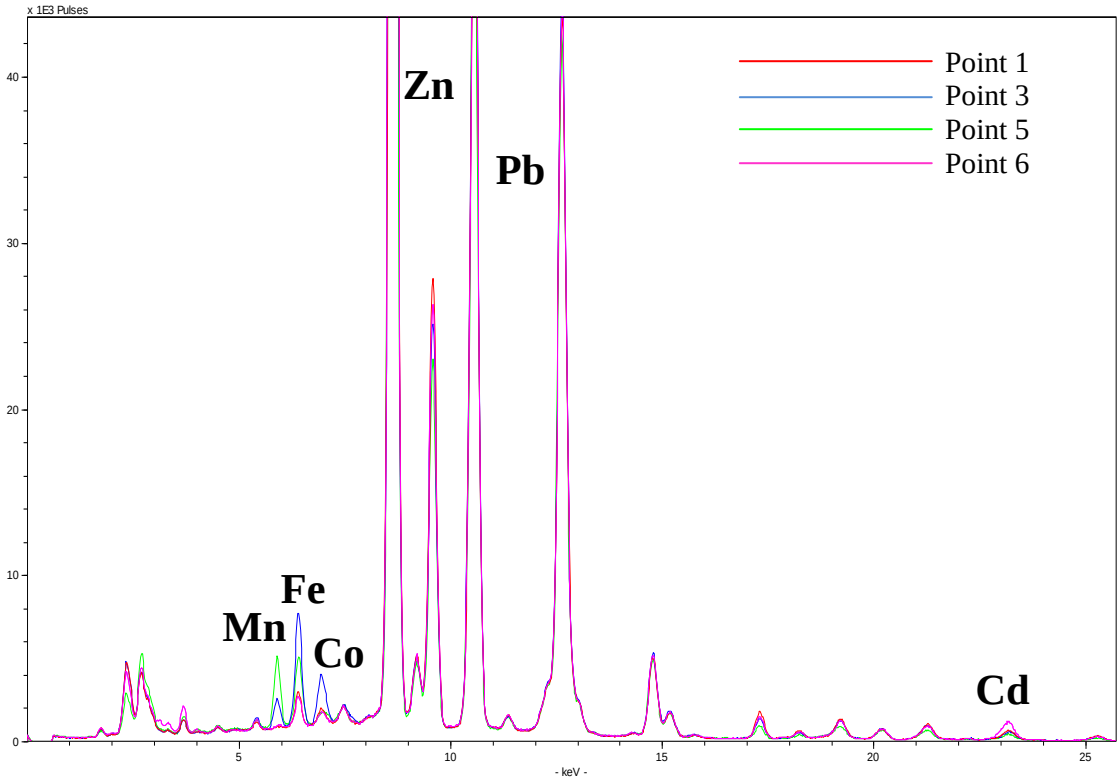

Figure 182. *Bluebonnets on a Texas Landscape*. Point 1, white, compared to points 3, 5, and 6, reddish browns.

Blue

The blue of point 8, the blue of the sky, has a peak for cobalt and tin, indicating that the sky is cerulean blue. The blue of point 4, the dark blue of the bluebonnets, has a much more distinct peak for cobalt, but no peak for tin (figure 183). It is a cobalt based blue, but if it is cobalt blue, which is cobalt doped alumina, the aluminum peak is not visible.

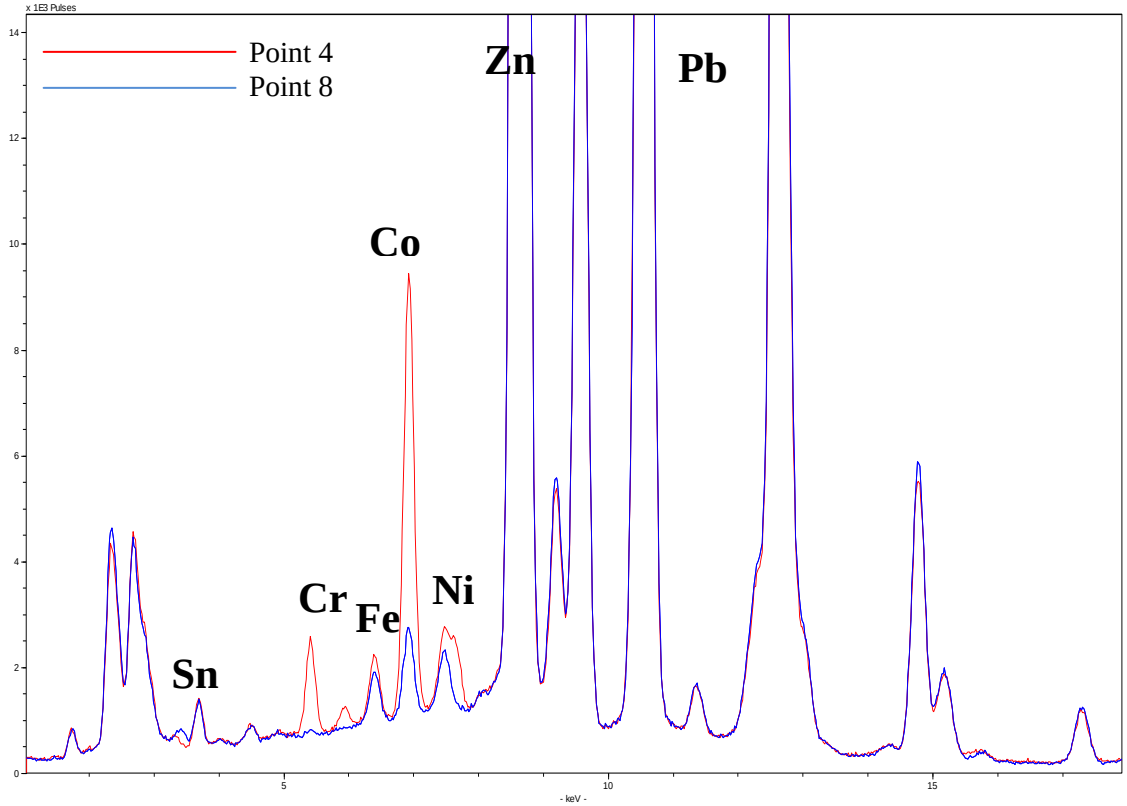

Figure 183. *Bluebonnets on a Texas Landscape*. Points 4 and 8, blues.

Late Afternoon in the Lupine

Figure 184. *Late Afternoon in the Lupine.* No Date, Signed Julian Onderdonk, Oil on Board, 6in x 9in, Witte Museum, San Antonio, TX.

A total of five points were analyzed for *Late afternoon in the Lupine* (figure 184), a small study on a wood board Onderdonk made for a larger painting. Point 1 is violet, point 2 is blue, point 3 is green, point 4 is the off white of the sky, and point 5 is the red of a tree to the right of the painting.

Blue, Red and Violet

Points 1 and 2, the violet and the blue of the bluebonnets both derive their blue color from the presence of cobalt and tin, indicating cerulean blue. The violet appears to be a blend of red and blue, and not a stand-alone violet. Comparing the red, blue and violet points to point 4, the white of the sky, it is apparent that the white for the sky is zinc based and not lead based (figure 185). The highest peak for lead in the painting is from point 5, the red of the tree. This suggests the use of red lead. Likewise, both the blue and the violet have high peaks for lead, and therefore point 1, the violet, was most likely made by mixing the cerulean blue and the red lead.

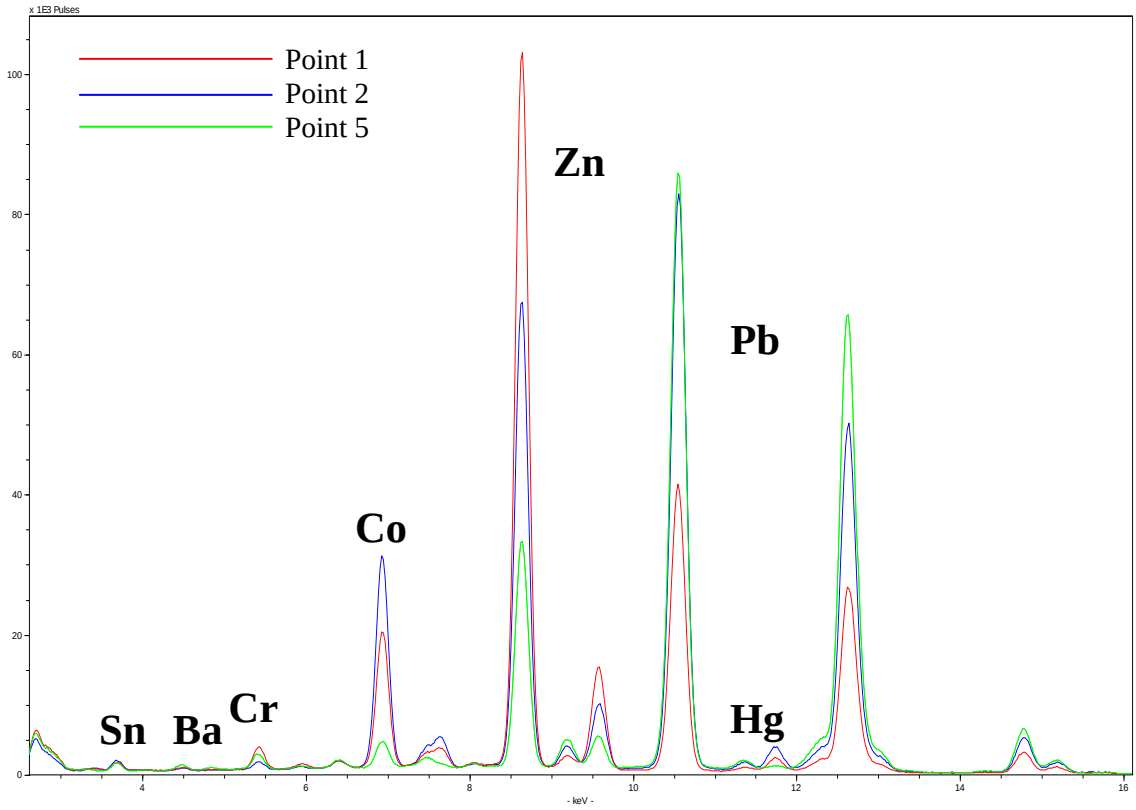

Figure 185. *Late Afternoon in the Lupine*. Point 1, violet, compared to point 2, blue, and point 5, red.

Green, White, and Yellow

The green of point 3 has the highest peak for chromium in the painting, indicating the use of chromium oxide green (figure 186). There are also distinct peaks for cadmium and sulfur, which points to the use of cadmium yellow as a lightener. This is interesting given that the spectrum for point 4, the yellow white of the sky, is predominately zinc with peaks for barium and chromium, which would suggest that the sky is zinc white mixed with the barium-based lemon yellow. Barium can also be used for a white ($BaSO_4$), but the point in the sky lacked the peak for sulfur that the point green point had. Point 4 also has a peak for copper, an element not seen in the rest of the painting. Copper can be used for blues or greens, and there is a hazy blue mixed in the clouds, so it appears that copper was also used for blue alongside cobalt.

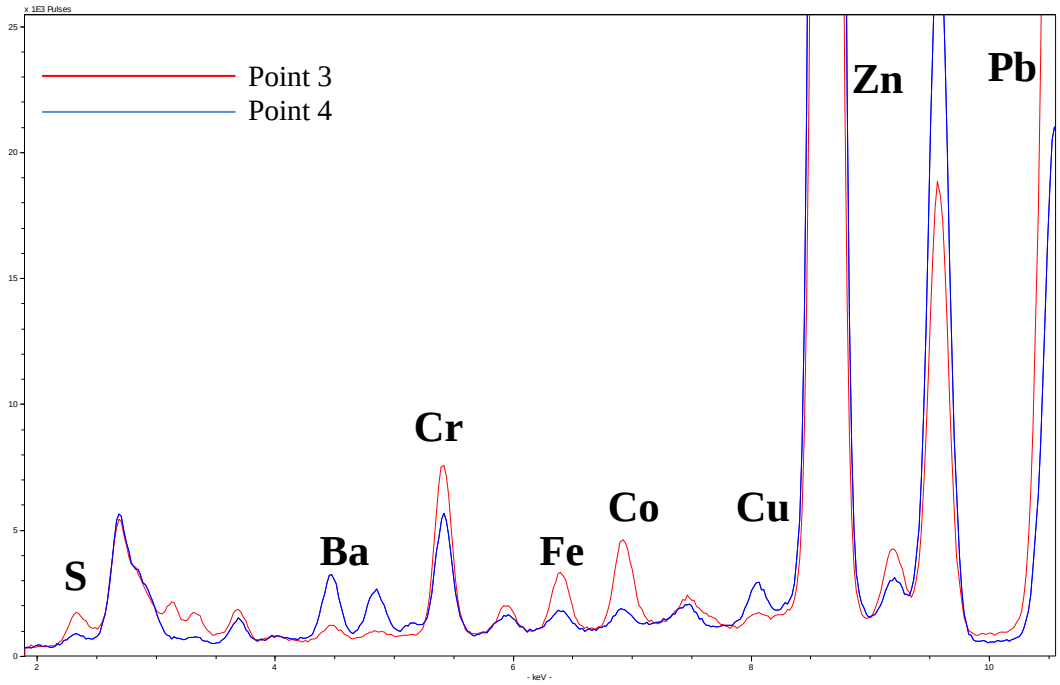

Figure 186. *Late Afternoon in the Lupine*. Point 3, green, compared to point 4, yellow.

SECTION 8: CROSS PAINTING ANALYSIS

Table 3 below lists each painting with a known date and the characteristic elements for each hue analyzed, with the exception of *Bluebonnets in San Antonio* due to the prevalence of titanium in each point analyzed, and *Milkweed in Bandera* due to the lack of conclusive data. Based on this chart, several overarching patterns about pigment preference can be determined. Looking at the primer and the whites, it appears that Onderdonk did not use zinc white until after he moved back to Texas in 1909; this is likely not true given further analysis below. Regardless, his preference for zinc white grew, and by 1914 it seems he had phased the lead white out of use almost entirely until he re-introduced it in 1921. He seems to have eliminated mercuric red pigment by 1908, though it does show up again in the 1922 *Dawn in the Hills*. In 1909 there was a shift away from iron-based blues to cobalt-based blues, along with a shift from zinc-based yellows to cadmium-based yellows.

Painting	Year	Primer	White	Red	Yellow	Green	Blue	Brown
Sunset November 1899	1899	Pb	Pb	Fe	Zn	Cu	Org/Cu	
Sand Dunes	1901	Pb	Pb	Fe/As	Zn / Ba	Cu	Fe	
Cock Fight Amid the Jacals	1905	Pb	Pb	Hg	Fe / Sr	Cr	Org	Fe
Portrait of G. Beddle Moore	1905	Pb	Pb	Hg	Zn / Ba			Mn/Fe
Harbor Scene	1906	Pb	Pb	Hg			Fe	Fe
October Sullivan Co. NY	1908	Pb	Pb	Fe	Zn	Cr	Org /Fe	
A June Morning	1909	Pb	Pb	Fe	Zn / Ba	Cr	Fe	
Family at Cards	1909	Pb	Pb	Fe	Zn / Cd		Co	
Bluebonnets and Cacti	1910	Zn / Pb	Zn / Pb	Fe	Sr / Cd	Cr	Co / Fe	
Bluebonnet Field	1912	Pb	Pb	Fe	Cd	Cr	Co / Sn	
A Pool on the Guadeloupe	1913	Pb	Zn / Pb	Fe	Zn	Cr	Co / Sn	
Afternoon Back of Laurel Heights	1913	Pb	Zn / Pb	Fe	Zn / Cd	Cr	Co	
Evening in the Bluebonnets	1914	Zn	Zn	Pb / Fe	Cd	Cr	Co / Sn	
Texas Mountains on Williams Ranch	1915	Zn	Zn / Ti	Pb / Fe	Cd		Co / Sn	
Williams Ranch, 20 West of Kerrville TX, near Junction	1915	Zn	Zn	Pb / Fe	Cd	Cr	Co	
Late Afternoon Sunlight on the Bluebonnets	1916	Zn	Zn	Fe	Cd	Cr	Co / Sn	
Bluebonnets at Sunset San Antonio	1919-20	Zn	Zn	Fe	Ba / Sr		Co / Sn	
A White Road at Late Afternoon	1921	Zn	Zn	Pb / Fe	Ba / Sr	Cr	Co	
Miles and Miles of Bluebonnets	1921	Zn	Pb	Fe	Sr	Cr	Co	

Table 3. Dated paintings and their primary elemental constituents for each color.

Using this chart as a stepping off point for spectral comparisons between paintings, the primary elemental constituents of the undated paintings are listed in table 4; using these two tables, the elemental composition of the dated paintings were compared to the undated paintings to see which paintings fit with which date range the best. Several paintings illustrate shortcomings in the date ranges derived from the dated paintings; *At the Edge of the Forest* fits best with the 1909 range of pigments, but the inclusion of mercury hints that Onderdonk continued to use mercuric red throughout his

entire time in New York instead of stopping in 1906. Likewise, *Seascape V*, signed Chas. Turner, fits best with the dates of 1905-1908, and if this is correct, the supposition that zinc whites were not introduced until 1909 must be incorrect.

Painting	Primer	White	Red	Yellow	Green	Blue	Brown
Pastoral with Lady in Red	Pb	Pb	Hg / Fe	Ba	Cr	Fe	Mn / Fe
Seascape V	Pb / Zn	Pb / Zn	Hg /Fe	Ba	Cr	Org	
Landscape with Cacti	Zn	Zn	Pb	Cd	Cr	Co	
A Man Fishing From a Boat	Pb	Pb	Fe / Hg	Zn/Ba	Cr	Cu	
At the Edge of the Forest	Pb	Pb	Hg / Fe	Cd/ Zn	Cr		
Central Park	Pb	Pb	Fe	Cd	Cr		Fe
Fall Landscape #2	Pb	Pb	Hg	Ba/Sr/Zn	Cr	Cu	
Large Bluebonnet Landscape	Zn	Pb	Fe / As	Cr/Sr	Cr	Cu / Co	
Summer Afternoon	Pb	Zn / Ba	Fe		Cr	Org	Mn
Bluebonnet on a Texas Landscape	Zn	Pb	Fe	Cd	Cr	Co / Sn	Mn
Study - Lupine	Zn	Zn	Pb	Cd/ Ba Sr	Cr	Cu / Co	

Table 4. Undated paintings and their primary elemental constituents for each color.

Despite these shortcomings, the compositions of several of the undated paintings match very well with the dated paintings. *Pastoral with Lady in Red* looks very much like *Cock Fight Amid the Jacals* and *Portrait of G. Beddle Moore*, and it is likely that it was painted around 1905. Table 5 lists the undated paintings with their most parsimonious compositional match to the dated works. To further substantiate the matches made via the elemental composition, the undated paintings were crosschecked with the signature analysis of selected paintings carried out by James Baker in Julian Onderdonk in New York: The Lost Years – The Lost Paintings (2014, 165-168).

Painting	Assigned Date Range	Basis	Signature Estimated Date
Pastoral with Lady in Red	1905	Pb white, Hg red, Fe blue, Mn brown	
Seascape V	1905-1908	Hg red, Org Blue, Ba yellow	
Landscape with Cacti	1910-1915	Zn white, Pb red, Co blue	
A Man Fishing From a Boat	1905	Zn/Ba yellow, Hg red, Pb white	1905
At the Edge of the Forest	1909*	Pb white, Cd yellow	
Central Park	1909-1912	Pb white, Fe red, Cd yellow	Post 1906-1908
Fall Landscape #2	1899-1906	Pb white, Hg red, Zn yellow, Cu blue	1905-1908
Large Bluebonnet Landscape	1910	Pband Zn white, Fe red, Sr yellow, Co blue	Post 1906-1908
Summer Afternoon	1905	Org blue, Mn brown	Pre 1908
Bluebonnet on a Texas Landscape	1910-1913	Pb and Zn white, Fe red, Cd yellow, Co and Sn blue, Mn brown	1910
Study - Lupine	1915-1920	Zn white, Pb red, Ba and Sr yellow, Co blue	

Table 5. Undated paintings and their assigned date ranges based on spectral similarities with dated paintings.

* The inclusion of Hg red could suggest an older date, but *Seascape V* supports a 1909 date.

There were no conflicts between the assigned date ranges and the signature estimated dates, which, if nothing else is at least encouraging. Looking at the ranges of when these pigments were used, an unexpected question is raised. Onderdonk's fatal illness was said to be sudden, and he died in the hospital after emergency surgery. Looking at his 1921 and 1922 paintings, it seems that Onderdonk shifted back towards using the more toxic pigments after a long hiatus; is it possible that this shift back was related to his sudden decline in health? A series of studies in the United States based on the 1904 work of John Lockhart Gibson exposed the dangers of lead-based household paints to children, and in 1912 British scientists Kenneth Goadby and Thomas Legge

published the well-known treatise *Lead Poisoning and Lead Absorption* in the United Kingdom (Riva et al 2012). The scientific evidence and the growing concern over health implications of lead poisoning in the early 20th century led to an increase in government regulation restricting the use of lead paint in both artistic and home use by the 1920s. (Riva et al 2012). The time frame for these studies coincides with the sudden cessation of lead white in Onderdonk's work, though oddly he appears to have begun using red lead, or minium, around the same time he stopped using lead white. He also appears to have used mercuric red for the first time in over a decade with *Dawn in the Hills*, the last painting he worked on before he died. Mercury poisoning is cumulative, and it is unlikely a single exposure late in his life would have been a significant factor in his demise, but it does seem a curious choice. Could a shift back to toxic paints have played a part in Julian Onderdonk's untimely death? Obviously many more paintings would need to be examined to reach this conclusion, and apart from mentioning this for the sake of novelty, it is somewhat beside the point of this study.

SECTION 9: CONCLUSIONS AND FUTURE WORK

Despite the inability to directly determine the chemical bonds of elements in a material using XRF, with enough data points and a moderately restricted pool of possible chemical formulas, it is entirely possible to establish the chemical makeup of cultural resources like art and archaeological artifacts. With the work of Julian Onderdonk, clear patterns of changing pigment preferences through time revealed themselves when each of the paintings was analyzed. It has been shown that undated works can be reasonably associated with the spectral signatures of dated works, allowing for a completely non-destructive way to categorize the undated works into the various phases of Onderdonk's career. It has also been shown that by establishing these patterns, paintings incorrectly attributed to an artist can be discovered, as is most likely the case with *Bluebonnets in San Antonio*.

Titanium white was observed in single areas in four paintings, two of which, *Bluebonnet Landscape* and *Man Fishing from Boat*, were examined under black lights and observed to have been restored. The other two, *Miles and Miles of Bluebonnets* and *At the Edge of the Forest*, will need to be analyzed under black lights in the future to verify the assessment that they too have undergone restoration, but the lack of a consistent pattern of titanium throughout the painting strongly suggests as much.

The aim of this study was to utilize a portable non-destructive analysis technique to expand the knowledge available about a collection of cultural heritage materials. The results of the technique outlined here have proven to be very satisfactory in achieving this aim, though clearly refinements in instrumentation would be advantageous. Future

studies incorporating the use of analytic methods capable of detecting organic materials and the chemical bonds between the elements detected would greatly enhance the breadth and depth of the results outlined in this study. However, given that the pXRF was easily transported to the various locations of the paintings and obtained excellent data sets without any adverse effects on these priceless works of art, this was an overall worthwhile endeavor.

Going forward, by utilizing the same techniques for identifying pigments established and outlined in this thesis, a recent study of Native American rock art in Big Bend State Ranch Part was completed; the results will be available in a forthcoming publication. Further studies on various archaeological artifacts will continue to expand and elaborate on the knowledge we have about our shared cultural heritage.

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